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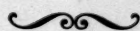
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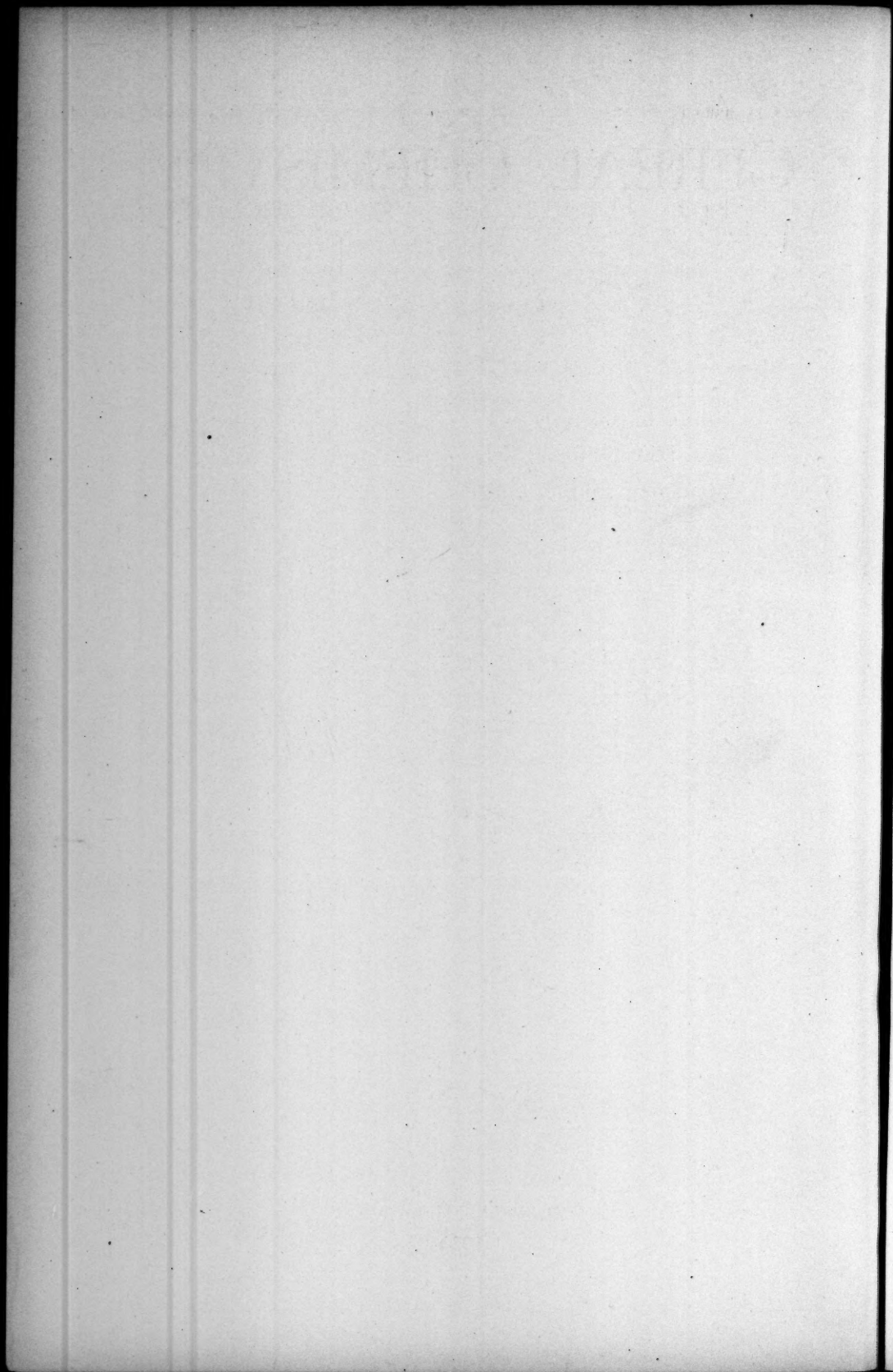
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**STALING OF BREAD**

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A fresh loaf of bread may be considered one that has stood long enough after baking to reach room temperature, or slightly above. Under usual conditions, this occurs in about two hours.

Among the chief characteristics of such bread are compressibility, elasticity, and the particular taste and odor that the consumer has become accustomed to consider desirable. The crumb of fresh bread is evidently not in equilibrium from several standpoints, as will be discussed later.

Many changes occur in such a loaf on aging, any or all of which may be important in fixing the acceptability of the bread to the consumer. The word "staling" is commonly considered as including all changes that occur to the finished loaf on storage under usual conditions, until consumed. The period of storage is seldom more than three days, and practically never more than a week.

The changes on staling are of several entirely different kinds, which normally occur simultaneously. They are, however, more or less independent of one another. Some of these changes may be accelerated or inhibited while the others are affected to a lesser or even negligible degree.

Changes that may take place in the staling of bread stored under normal conditions are:

1. Loss of volatile constituents, i.e., "evaporation losses."
2. Possible changes due to oxidation.
3. "Inherent staling," namely, changes that take place apart from losses or gains from the surroundings.

We shall examine each of these briefly in order.

1. Loss of *volatile constituents*, called here "evaporation losses." Bread contains several volatile constituents. Of these, water

overwhelmingly preponderates, making up, roughly, 38% of the weight of the finished loaf and much the greater part of all volatile ingredients. However, bread contains other volatile ingredients, all of which evaporate to some degree. These include  $\text{CO}_2$ , alcohol, volatile fatty acids, principally acetic (Johnson 1925), and minute traces of other volatile compounds. Many of these are probably of importance in contributing to the appetizing aroma of fresh bread that is noticeably absent in stale bread, their loss being an important factor in staleness as considered by the public.

It is evident that evaporation losses can be entirely prevented by sealing the bread in a closed container, or they may be greatly retarded by cold. It is significant that those who have experimented with the effect of cold on bread—Berg and Morison (1925), Glabau and Pirrie (1925), Berg (1926, 1929), Katz (1928)—all comment on the improved flavor and odor of bread stored at low temperature. Evidently the evaporation of the volatile products associated with the aroma of fresh bread has been greatly diminished. The effect of cold in retarding oxidation is probably negligible in such a short time. Evaporation losses may be accelerated by subjecting the bread to vacuum or a current of gas.\* The loss of any one or more of the known volatile constituents may be lessened or prevented by subjecting the bread to an atmosphere saturated with the vapor of this constituent. The action may even be reversed by subjecting the bread to an atmosphere of any given constituents having a partial pressure of these constituents greater than that of the bread.

It is evident that these evaporation losses are easy to measure and to control experimentally (even if not commercially); and that such control may be exercised independently of other staling factors.

Among volatile organic products most work has perhaps been done on alcohol (Sundberg, 1923, and Lindet, 1926). Sundberg found up to 0.47% alcohol in fresh bread. He found that on staling this amount diminished to zero, the loss depending on both age and amount of exposure. He reports aldehydes (undetermined as to kind or quantity) present in the steam distillate of the bread.

Lehmann (1902) has shown a slight decrease in the titratable acidity of bread on staling, and Karácsonyi (1928) a slight decrease in hydrogen-ion concentration. Barnard and Bishop (1914) and White (1910) have shown that an increase in acidity is due to the activity of micro-organisms after baking.

2. Changes due to oxidation. It is known experimentally that other baked products and also many other foods take up oxygen on storage. In biscuit and crackers, for example, the fat will eventually take up oxygen, giving a pronounced tallowy odor. Many foods, substantially free from fat will likewise take up oxygen, giving a weaker but quite definite "stale" taste. Many experimenters, including the writer, have shown that these changes in taste could be entirely prevented by storing such foods in air-tight containers. Oxidation is probably of minor importance in the staling of bread, owing to the relatively short period of storage.

Schibsted (1929) has experimented with the  $O_2$  absorption of bread. The method consisted in cutting bread at  $28^\circ C.$  about four hours after baking, into  $\frac{1}{2}$  inch cubes and immediately sealing these in air-tight tin cans so that the cans were substantially full. These cans were stored at room temperature.

Determinations of  $O_2$  absorbed were made each day by washing out the air in the bread-filled can by passing a stream of  $CO_2$  through the can. The  $CO_2$  is absorbed in KOH solution and the residual air collected in a gas burette. The proportion of  $N_2:O_2$  is determined by the usual methods of gas analysis. The deficiency in the normal proportion of  $O_2$  indicates the amount of  $O_2$  absorbed.

Results of one series of tests showed 2.45 cc. of  $O_2$  absorbed per 100 gm. of bread in the first 36 hours and 2.25 cc. more in the following 24 hours. At the end of this period, by examining this bread macroscopically and by smelling and tasting, no evidence of souring or molding was discerned. During the next 24-hour period, however, all the  $O_2$  in the can had disappeared and the bread was found to be distinctly moldy. Probably at least part of the  $O_2$  absorption in the previous periods was due to the action of mold before its growth had become evident to the senses.

Bread sterilized in cans at 15 pounds steam pressure for 30 minutes took up a little  $O_2$  during sterilization, but the rate of oxidation thereafter was negligible over the period studied (three weeks). This bread did not develop mold or show other evidence of microbiological action.

Bread stored in an atmosphere of  $CO_2$  absorbed this gas comparatively rapidly, being similar in this respect to several other food products.

Wahl (1915) attaches great importance to the influence of oxidation on staling. He says in his patent specifications: "The undesirable effect of oxygen upon the flavor of delicate nitrogenous

foods has been fully demonstrated in the brewing industry, and my experience leads me to believe that bread becomes stale largely by reason of the oxidation caused by the drawing in of air." He states elsewhere in his specifications: "I have discovered that if the bread be cooled in an atmosphere of carbon dioxide, the bread is thereby so much modified as not to become stale, but on the contrary remains fresh for a long time after baking."

To test this point, we packed two air-tight drums, holding 28 loaves each, with bread immediately after it was taken from the oven. One of the drums was thoroly flushed with a stream of  $\text{CO}_2$  and a small stream of  $\text{CO}_2$  was then conducted through it for 36 hours. The bread was examined at intervals by tasting and the inherent staleness was measured by the compressibility apparatus, described later in this paper. There was little difference between the taste of the bread stored in  $\text{CO}_2$  and air, respectively, the advantage, if any, lying with the bread cooled in air. Measurements of inherent staling, on the apparatus described in this paper showed that both lots of bread exhibited the characteristic change in compressibility of the crumb. We did not find a significant difference in rate of staling between the  $\text{CO}_2$ -treated and the air-treated loaves.

For the short time that bread is commonly stored, and during which the greater part of the staling phenomena is known to occur, we therefore do not find any important effect from excluding air and substituting  $\text{CO}_2$ .  $\text{CO}_2$  will check the growth of molds on longer storage.

3. Inherent staling, changes that take place in the bread apart from losses or gains from its surroundings.

It is well known that certain complicated changes take place in bread during storage, in addition to those connected with evaporation losses or oxidation. This was recognized as long ago as 1853, by Boussingault. These changes are distinct from evaporation losses or oxidation. In spite of this, they are much confused with moisture loss, by the public and even by some authors. In order to distinguish such changes, I have called them "inherent staling" (for want of a better name) as these changes are inherent in the bread itself, and occur even in the absence of any gain or loss of material from the outside.

"Inherent staling" doubtless involves several simultaneous processes, some of which are understood and others are not. The changes of inherent staling are measurable and controllable to a lesser extent than evaporation and oxidation changes. The crumb



of fresh bread represents a system that is not in equilibrium. The lack of equilibrium is brought about to some extent by the fact that the bread has been heated to nearly 100° C., and the concentrated gel of which it is constituted has not had time to reach equilibrium at room temperature, possibly due in part to the formation of a supersaturated solution of some ingredients on cooling. Inherent staling, therefore, is in part simply the approach of the bread crumb to the equilibrium at the new temperature at which it is held while aging. As has been shown, these processes may be reversed by changing the holding temperature.

Under certain conditions, microbiological changes may occur in bread after baking, for example, the growth of mold or rope. Such changes do not occur to a noticeable degree in bread properly fermented, baked, and stored. They are not ordinarily considered as coming under the term "staling." They may, in fact, be considered as pathological, and are excluded from present discussion. (See Barnard and Bishop, 1914; Morison and Collatz, 1921; Streider and McClellan, 1922.)

The processes connected with the staling of bread are of great scientific interest and tremendous importance. Davis and Eldred (1923), of the Food Research Institute, state in their comprehensive survey of this problem:

"Practical bakers know well that loaves made in different ways have different keeping qualities. Thus loaves made simply from flour, water, salt and yeast, especially if the fermentation has been carried out rapidly, are believed to grow stale faster than loaves made with milk, shortening and other additions, especially if the fermentation has been conducted more slowly. A number of baking companies have learned to understand the process sufficiently to produce loaves which keep much longer than most bakers' bread. Apparently, however, there have been no careful and adequate investigations which make it possible to offer a scientific explanation for differences in keeping quality observed in loaves made by different formulae and by different bakeshop practices. Such investigations are urgently needed. . . .

*"In our judgment, there is hardly another single point on which a baker may well lay more stress. . . .*

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<sup>1</sup> Italics are ours.



"The keeping quality of the loaf is of such importance, both to the baker and to the consumer, that it is surprising that this feature has not been given direct consideration in drafting 'score cards' for bread. . . . Even before a scientific basis for the analysis of keeping quality can be developed, this point should be given considerable weight among the features of a standard loaf. We believe that high keeping quality will prove, in the long run, one of the most important factors in putting bakers' bread generally on a par with the best home-baked bread."

It is a matter of general experience that some bread has much greater keeping qualities than other bread; that is, under given conditions grows stale much more slowly. Whympers (1920) states: "The effect of freshness can be enormously increased and sustained by the addition of small quantities of fat. . . . The use of one-half milk and one-half water instead of all water as liquor has a somewhat similar effect and the bread produced from this mixing recalls the homemade farm loaf which does not appear to change from the original state of freshness for a week or more if kept in a cool dry place."

Other factors thought to deter staling are: (a) The long sponge system compared with the short dough fermentation system (Kent-Jones, 1927); (b) small quantities of yeast and correspondingly long times of fermentation (Katz, 1915); (c) salt (Katz, 1915); (d) good quality of gluten (Dearsley, 1925); (e) milk (Davis and Eldred, 1923; American Institute of Baking, 1924).

On the other hand, Whympers (1919) and Katz (1928) mention several substances, such as glycerine, supposed to retard staling, which are now generally discredited for this purpose.

The action of volatile aldehydes and alkaline substances, discovered by Katz (1915 and 1928) is mentioned later in this paper. There is, also, a British patent (1922) for keeping bread fresh through the addition of a soluble peroxide.

In the staling of bread, there is a transfer of water from the crumb to the crust. In this paper interest is concentrated on the changes that occur in the crumb. The crust of bread is a layer of such uncertain thickness and varies so tremendously even in the same loaf, that quantitative measurements are necessarily unsatisfactory.

### Review of the Literature

As long ago as 1853, Boussingault (*loc. cit.*) published some experiments on the staling of bread that are remarkable for their clear exposition of the factors involved. Boussingault distinguished clearly between the hardening of the bread due to evaporation and that due to what I have called "inherent staling," showing that the latter was the more important and took place even when evaporation was eliminated by storing the bread in hermetically sealed containers. He pointed out that inherent staling proceeded at a slower rate at high temperatures, 50°-60°C. He showed also that the inherent staling changes could be reversed by raising the temperature of bread that had cooled and become stale, and described the transfer of moisture from the crumb to the crust.

Among other early workers, Balland (1892) showed that the swelling power of bread in water decreases during staling.

The other principal phenomena connected with inherent staling have been described remarkably clearly by the early workers. An extensive survey is given by Maurizio (1924). The literature has been summarized by Ostwald and Lüers (1919). I have somewhat elaborated their summary as follows:

1. According to Lehmann (1904) and Katz (1915), in inherent staling, the starch plays the most important part, and the protein a minor part. However, starch gels are relatively easy to study, and they exhibit changes of stiffening and syneresis on standing that have been considered analogous to the changes in bread. The changes in a coagulated protein network such as exists in bread are evidently much harder to study, hence the emphasis in the study of staling has been placed on the starch. In so doing it is probable that other changes occurring in bread have been neglected. (See Alsberg and Griffing, 1927, and Alsberg, 1928.)

2. If soaked in an excess of water, stale bread will swell less than fresh bread (Lindet 1902, and Lehmann, 1904). Katz (1915) made this observation the basis of one of his methods for measuring the staleness of bread.

3. The pore volume of stale bread is noticeably greater than that of fresh bread (Lehmann, *loc. cit.*). This is connected with the microscopic appearance as reported by Verschaffelt and van Teutem (1915). They report that in bread in which inherent staling has taken place the starch grains appear to have a bolder outline, and an air space can sometimes be seen between the starch and the gluten.

4. The amount of polysaccharide extractable with water is greater for fresh bread than for stale bread (Lindet, 1902). Katz made this fact the basis of another method for measuring the staleness of bread, as we shall discuss later.

### Effect of Temperature

The rate of inherent staling is known to be dependent on the temperature. Above 60°C. there is little noticeable change in inherent staleness of the crumb on standing even 48 hours (Bous-singault, 1853). Katz (1917) worked on a commercial method of keeping bread fresh by maintaining the bread hot in an atmosphere of the proper humidity.

The rate of inherent staling increases rapidly to a maximum at 2° to 3° C. Below this, the rate becomes less, due possibly to a freezing out of the water, thereby inhibiting further change.

Studies have recently been made of the effect of cold on the keeping quality (i.e., rate of staling) of bread. The effect of cold on the odor, taste, and loss of weight are also recorded. Berg (1926) reports work on cooling bread on a large scale under commercial conditions on conveyors and racks; also on a smaller scale under experimental conditions, where temperature and humidity of the atmosphere surrounding the bread could be closely controlled. For rack cooling he found the temperature of the center of a loaf direct from the oven to be 97° C., and that nearly two hours was required to cool a 1 pound or 1½ pound loaf to 35°, the safe temperature for wrapping. The surrounding atmosphere was 38° to 29° C., and the relative humidity about 50%, with a loss in weight by the loaf of 3.48 to 4.23%. On the other hand, similar bread in a special cooler required only 49 minutes to cool, with a loss of weight of 1.74%. Here the surrounding atmosphere was 7°, and the relative humidity 72%. Berg states: "It was observed that after cooling at low temperatures the bread did not appear soggy. It was, also, noted that after 24 to 36 hours, wrapped bread cooled at a low temperature in the cooler possessed a better flavor, somewhat better character of crust, and appeared fresher than bread cooled on a rack in the shop." The author also states: "A method which prevents rapid loss of moisture in bread should retard staling." No actual measurement of the rates of staling of loaves cooled in various ways were made. Such quantitative measurements of staling would have added considerably to the value of this interesting work.



Tests were carried out, also, by the American Society of Bakery Engineers (Berg, 1929) on "The Keeping Quality, Odor and Taste of Bread Wrapped at Different Temperatures." Bread was cooled in four different ways before wrapping, namely, hot (average temperature  $46^{\circ}\text{C}$ ., average cooling time 50 minutes); medium hot (average temperature  $38^{\circ}\text{C}$ ., average cooling time 74 minutes); cool (average temperature  $30^{\circ}\text{C}$ ., average cooling time 114 minutes); ice box (average temperature  $31^{\circ}\text{C}$ ., average cooling time 64 minutes). The temperatures given are those of the centers of the loaves at the time of wrapping. All experiments were carried out in commercial bakeries, and in the first three the cooling was on racks. The judges considered that the bread wrapped warm had the best keeping qualities; that cooled in the ice box, second best, and that wrapped cool, the poorest. Here, again, judgments were rendered on the basis of examination without any attempts at quantitative determination of the rate of staling of the different loaves. The judgment as to keeping qualities is conflicting and is not significant when subjected to statistical analysis.

Two other reports on the effect of cold on the keeping qualities of bread may be mentioned. A test was made by Berg and Morison (1925) in which bread aged outdoors at  $-2^{\circ}$  to  $-20^{\circ}\text{C}$ . was compared with that aged indoors at room temperature. The bread exposed to the cold was thought to have a better flavor and taste and to be the fresher of the two. Glabau and Pirrie (1925) report somewhat similar observations, concluding: "If the loaf can be maintained under conditions whereby it does not actually freeze, but merely becomes cold, by being protected from freezing, then it would appear that the qualities of the loaf are enhanced in that it remains softer for a longer period, and the flavor may be improved." The latter conclusion is contrary to the theory of Katz, who claims that the temperature near freezing is that of maximum rate of staling. In neither of these instances were any measurements of staleness made.

### Reversibility

Another fact that has been known for a long time is that the changes occurring in inherent staling are reversible with heat. This, too, was pointed out as long ago as 1853 by Boussingault (*loc. cit.*) who effected this reversal several times on the same piece of bread crumb. This fact is of great theoretical interest. Staling has been compared to the so-called retrogradation of starch

pastes. Retrogradation, however, is irreversible, so it seems that inherent staling cannot be explained merely as a retrogradation of the starch taking place within the crumb of baked bread. This objection has been pointed out by Alsberg (1928) and others.

The greatest amount of recent work on the staling of bread has been done by Katz. His results are published in full only in the Dutch language (Katz, 1917). The two volumes of this work have been out of print for some time and are extremely difficult to obtain. (Copies may be found at the New York Public Library.) Summaries of his work are available, however, in German (Katz, 1913, 1915).

Very recently, and since the beginning of this investigation, Katz (1928) has published in English a summary of his earlier work. Altho this summary contains an excellent general review of his work, many points of interest contained in the original Dutch book are necessarily omitted. Some of these points, therefore, seem worth quoting.

#### **Quantitative Measurement of Inherent Staling**

Besides elaborating and confirming much of the work of the earlier writers mentioned, Katz set about the difficult task of finding a quantitative method for measuring the inherent staleness of bread.

His methods are as follows: (given in a different order from his own.)

**Extractable polysaccharides.**—Katz has consistently looked at inherent staling as primarily a change in the starch. For this reason he naturally turned to a determination of the polysaccharides extractable in water and insoluble in alcohol as a promising means for measuring staleness. His method is described in his chapter in Walton's book already referred to (Katz, 1928).

By following, each time, exactly the same method of procedure he was able to secure fairly consistent results. He reports many results, all of which show a decrease in the water-extractable alcohol-insoluble polysaccharides that is roughly proportional to the degree of inherent staling as determined by other methods.

An example of the differences between fresh and stale bread noted by this method (and by other methods) is shown in Table I, quoted from Katz (1915).

Several objections to this method are evident. (1) It is the most time-consuming of the three methods advocated, tho the



time required is by no means excessive compared with other analytical methods. (2) Other carbohydrates in the bread contribute to these results besides those derived from the wheat starch. These might be, for example, dextrins contained in any malt extract used, and especially lactose from milk. The effect of lactose is shown by a comparison of Katz' figures in the same paper for milk bread and water bread. The second objection is, however, not important. What is of interest in any determination on staling is a comparison of figures for *the same type of bread* when fresh, and after aging under various conditions.

TABLE I\*

Age of bread hr.	Crumbliness	Hardness†	Swelling power	Water-soluble amylose‡
1	Not crumbly	0.240	53 } 52½	3.85 } 3.81
			51½	3.76
3	" "	.150	47 } 46½	3.65 } 3.67
			46	3.68
6	" "	.106	44 } 44½	3.65 } 3.65
			45	3.65
9	" "	.090	40½ } 41	3.45 } 3.43
			41	3.38
12	First beginning	.076	39 } 39½	3.36 } 3.34
			40	3.31
24	Very crumbly	.044	36 } 36½	3.20 } 3.15
			36½	3.09
48	More so	0.030	34½ } 34½	2.94 } 2.91
			34½	2.87

\*From Katz, 1915.

†Bread must be well cooled or the drop in the first hour will be too great.

‡After subtracting protein.

A fundamental objection to this method is that it does not show all of the alcohol-insoluble polysaccharides that are extractable with water, or nearly all of them, or any definite part of them. The amount determined depends upon the vigor of the method used for extraction and the time of standing.

A translation from Katz' original work in Dutch (1917) regarding this method is as follows:

"At first I had great expectations from this method. . . . However, the results of the experiments were disappointing. Instead of being accurate, the method appeared to be highly inaccurate. The values ordinarily showed discrepancies . . . making an uncertainty of 10% in the degree of staleness . . . I gave myself great trouble in trying to improve the method, but the desired result was not obtained. I have also tried to use the aqueous extract from the bread that was rubbed through the silk gauze in the determination of the imbibing power, but obtained

less regular results. It soon appeared that the errors were due mostly to the extraction. . . . More recently I have become inclined to believe that the difficulties are not simply to be ascribed to insufficiencies in the methods of analysis, but also to irregularities in the bread."

From a theoretical point of view, it is evident that the amount of polysaccharide given by this method may depend upon two factors: (1) The amount of such polysaccharide the bread contains; (2) the proportion of such polysaccharide that can be extracted from the unruptured starch grains by the method used. It is evident that the changes taking place on inherent staling may affect either or both of these factors.

Katz mentions that on fine grinding a large proportion of the contents of a starch grain becomes water soluble. The more recent work of Alsberg and Perry (1925) and of Alsberg (1926) not only confirms but places emphasis on this point, indicating that the change in the *extractability* of the polysaccharide may be the most important factor.

**Swelling power.**—Another method used by Katz for measuring the staleness of bread was a determination of the change in swelling power of the bread in water. This he carried out by rubbing the crumb of the bread through bolting cloth (80 meshes per cm.) with water, and allowing this to stand in a graduated cylinder for 24 hours. The volume of the decantate is then read off. The water is shaken again with the suspended crumb, and the sediment is allowed to stand another 24 hours, when another reading is taken. The average of the two readings is considered a measure of the swelling power of the starch. The water used is saturated with toluol to prevent bacterial action.

Katz notes the remarkable fact that the presence of a great excess of water fixes the degree of staleness of bread, and inhibits further staling. He demonstrates this by showing that there is no change in the swelling power of fresh and stale bread, respectively, on standing for four months under water preserved in various disinfectants.

In spite of this inhibition of the staling process by excess water, Peper (1926), a former co-worker, in continuing Katz' work, adds acetaldehyde to the water in which the bread crumb is suspended when he makes this determination. He says that he does this "in order to preserve the *status quo ante* of the starch." He evidently fears that some change in the staleness of the crumb may take

place even when suspended in water. Acetaldehyde is one of the substances that Katz found would inhibit inherent staling.

Katz (1917) says of the method of measuring the degree of inherent staleness by swelling power:

"When we wish to know the degree of staleness of a certain bread it is not of first importance to be able to determine the absolute value of the water-binding power. It is much more important that figures obtained in duplicate tests should agree as closely as possible. The closer this agreement, the greater the sharpness with which the degree of staleness of the bread may be expressed in figures. Under these circumstances, the method wherein the imbibing power is measured by measuring the volume of the settlings after 24 hours standing, appears to be the best. Although this method may appear at first sight to be primitive, it nevertheless yields satisfactory results."

Katz points out that the crumbliness of bread gives an excellent indication of staleness. He determined this condition by means of the finger, in which case he was doubtless also influenced by the softness of the bread. His attempts to measure crumbliness quantitatively were unsuccessful.

**Compressibility of crumb.**—A third method used for measuring the staleness of bread was a physical determination of what he calls the "hardness" of the crumb. In English, however, the word "compressibility" expresses better than "hardness" the characteristic of the crumb that Katz really measured.

The instrument used consisted of a metal ring, which lies flat upon the surface of the freshly cut loaf of bread to be tested "in such a manner that it rests all around upon the crust." This ring supports guides through which slides a rod that is perpendicular to the plane of the slice of bread. On the end of this rod is a plunger 22.5 mm. in diameter that rests upon the freshly cut surface of the bread. The plunger is weighted with 50 gm. When the plunger is released, it gradually sinks into the bread, the distance to which it sinks depending, naturally, upon the compressibility of the crumb. It will sink farther into fresh bread than into stale bread of the same kind. The plunger is allowed to act for three minutes, after which time its movement has practically ceased.

The descent of the plunger is indicated by means of a pointer on a dial, the movement being magnified five times.

Katz (1917) described this method as follows:

"The screw *i* serves to hold the rod fast during the loading

process in order to avoid application of any undesired pressure by means of the fingers. After the rod has been loaded the screw is loosened. The penetration thereupon occurs under uniform pressure.

"In order to ascertain the degree of accuracy attainable with this staleness-meter, I determined the penetration of the same bread at five different points. After each determination, a slice was quickly cut off and the determination repeated on the newly cut surface. In using the apparatus, the die was always placed as closely as possible on the central point of the sliced surface. The loaf itself and not the slice is taken for the test; otherwise, the hardness of the crust or of the support will influence the result. The result will be the more accurate, the more uniform the distribution of the holes in the bread; in other words, the more carefully the bread has been made."

The measurement of the inherent staleness of bread by a determination of the compressibility of the crumb seems to have the following advantages:

1. The determination is made on the bread *as it is*. The condition of the bread is not changed by grinding or rubbing or in any other way. No extraneous ingredient, such as water, acetaldehyde, or preservative, is added.

2. It determines the condition of the bread at a given instant under any desired conditions of temperature, etc. Possible changes such as those of bacteria, enzymes, chemical action, solution of certain ingredients in added water are excluded.

3. It is highly sensitive as compared with other methods. Using Katz' figures for the same bread (Table I), we find that the compressibility of fresh bread (0.240) is eight times the compressibility of bread 48 hours old (0.030). While the swelling power varies only from  $52\frac{1}{2}$  to  $34\frac{1}{2}$  cc., or 1.5 times, and the water-soluble amylose from 3.81 to 2.91 cc., or 1.3 times.

4. The determination on each loaf requires but two minutes. The result is obtained at once, compared with waiting 24 to 48 hours, as in the swelling method. Prompt results would make this method more useful for factory control.

5. The method is very simple, that is, the results obtained do not depend upon the development of an exact technic. This means that results from different bakeries obtained by different operators would be comparable. It can be carried out by an operator without scientific training.

As far as is known, no writer except Katz has worked exten-



sively with this method. Katz discontinued work by this method in favor of the swelling method, which he recommends in preference. Why this is so, is not clear.

Experiments with another method for measuring staleness have been published by Karácsonyi (1929). This method, which is evidently related to measurement of swelling power, consists in a determination of the viscosity of a suspension of the bread crumb in water. Good reproducibility was obtained.

Under ordinary conditions, the changes that take place in the staling of bread as shown by determinations of water-soluble amylose, swelling power of crumb, and compressibility of crumb, run roughly parallel. The development of crumbliness lags markedly behind. The same rough parallelism is exhibited when the staling process is inhibited or reversed by higher temperatures ( $60^{\circ}\text{C.}$ , for example). It has been shown, however, that these changes do not always proceed with equal velocity. For example, Katz (1915) showed that some substances, notably aldehydes and alkaline substances, had a marked inhibitory influence on the rate of inherent staling. This influence does not affect the soluble amylose, swelling power, and compressibility to the same degree.

### **Search for Underlying Causes**

There is fairly general agreement regarding the macroscopic phenomena that accompany the inherent staling of bread. There is much dispute and uncertainty regarding the chemical and colloidal changes underlying these phenomena.

Most investigators of inherent staling, both early and recent, have focussed their attention on the starch, partly because the changes in starch on heating are easier to follow chemically than those in the gluten network. The principal reason is that starch gels on cooling and aging exhibit phenomena that have some similarity to the staling of bread.

Starch chemistry, however, has until recently suffered from several fundamental causes of error. Alsberg (1926) pointed out that contradictory statements have persisted in the literature side by side for many years. The first, which is found in most textbooks, is that starch grains are completely ruptured on boiling in water. Whympers (1919) says: "Wheat starch in the presence of a sufficiency of water will commence gelatinization about  $60^{\circ}\text{C.}$ , and every granule will be completely burst at about  $65^{\circ}\text{C.}$ " The other statement (which turns out to be the true one) is that the starch grains swell tremendously and become almost transparent,



but do not actually burst on boiling. Failure to understand this has made unreliable many of the earlier determinations of the viscosity of starch pastes and the proportions of alpha and beta amylose.

The second cause of error has been the failure to recognize the important differences between different kinds of starch grains. These differences have been pointed out recently by Alsberg and Rask (1924) and Taylor (1928).

Potato starch differs considerably from other starches. Even the starches of the different cereals differ from one another in their action on boiling and in their chemical composition (Taylor, 1928). In a single grain of wheat, there are differences between the action of the large and the small starch granules.

When starch pastes age they become stiffer and an insoluble precipitate is formed. The speed of formation of this precipitate is accelerated by cooling. This change, called "retrogradation," bears some similarity to the inherent staling of bread, which is also believed to be accelerated by cooling. A number of writers have ascribed the process of bread staling to a retrogradation of the starch. Alsberg (1927) pointed out that bread staling differs from retrogradation, as above described, in the following important particulars: (1) In bread the ratio of starch to available water is 10:4, whereas in the starch pastes worked with the ratio is 10:40 or more. (2) The retrogradation observed takes place slowly (48 hours), whereas it is characteristic that the greater part of the inherent staling of bread takes place in less than 12 hours. (3) Retrogradation of starch is not reversible, whereas inherent staling is easily reversible with heat.

Staling has, also, been described (Ostwald and Lüers, 1919) as a syneresis comparable to the syneresis of dilute gelatin or agar gels. Syneresis resembles staling in that it is reversible with heating. Here again, however, the comparison does not seem to be exact, the difference being that syneresis as ordinarily known takes place only below a certain concentration of the gel, whereas in bread the gel is exceedingly concentrated.

Katz made some interesting experiments, heating starch with water in proportions and for times and temperatures comparable to those found in bread. It would be interesting to repeat these experiments, using, instead of pure water, a weak solution of sugar, salt, lactic acid,  $\text{CO}_2$ , diastase, etc., more like that found in a bread dough after fermentation. Possibly, also, the starch grains could be held slightly apart in a position somewhat comparable to

a bread dough by suspending them in an egg albumen solution aerated with  $\text{CO}_2$ , and then baking. The staling action of such a mixture, compared with the action of bread, would be interesting.

Alsberg and Griffing (1927) studied the condition of the gluten after baking. They call attention to the fact that it still has the property of swelling in dilute acid, and that it is far from an inert mass. They definitely state: "It may play an important rôle in the growing staling of bread." In this the author agrees, while admitting the great difficulty of isolating the effect of the gluten in order to study it.

Whymper (1919) published an interesting little book: "The Conditions that Govern Staleness in Bread." He worked on the lean formula used for bread in the British army. He uses a definition of staleness that is particularly inconvenient from the point of view of scientific treatment, and he is handicapped by the fact that he makes no quantitative measurement of staleness in connection with his experiments. His definition is interesting as a comparison with others. It is: "Staleness in a loaf may be said to have set in when, on placing in the mouth, the crumb feels dry and crumbly, requires a large amount of saliva to allow deglutition, and has not the sensation of dissolution as it passes from the mouth. These qualities of staleness are apart from flavor, which in fresh bread may be described as 'wheaty' or 'nutty' and in stale bread as insipid."

Whymper determined the total cold-water-soluble extract from bread and from a 4.3% starch paste. In both cases he obtained conflicting results, indicating again the uncertainties of this type of method. In general, he found, however, in both bread and starch paste, a decrease of soluble extract followed by a rise after about 100 hours.

An interesting experiment was the baking of three doughs made from 100 pounds of flour. The first was a normal control. To the second was added gluten from four pounds of flour, and to the third was added starch from four pounds of flour. The extra gluten loaf had good keeping qualities; the loaf with the added starch did not rise well, was white and opaque in appearance, of close, soggy texture, and grew stale much the fastest of the three, as judged organoleptically, but without actual measurements.

### Vapor Pressure

If staling is a syneresis by which part of the water held by the starch is released, it seems possible that the water so released

might increase the water vapor pressure of the bread on staling. To do this it was necessary to determine the vapor pressure of the bread in the presence of the air,  $\text{CO}_2$ , and other volatile constituents of the bread because evacuation of the bread might conceivably cause some change therein. We used, therefore, a dew point apparatus that was admirably adapted for this purpose. It is described by Cumming (1909). We found that the water vapor pressure of fresh bread did not differ from that of pure water within the limits of accuracy of the apparatus. No difference in the water vapor pressure could be detected between fresh bread and stale bread that had been stored so as to prevent loss of moisture. This confirms an earlier statement by Katz (1915).

### Rate of Evaporation of Moisture

Next I experimented with the rate of loss of moisture from fresh bread and from stale bread that had been stored so as to prevent loss of moisture. The fresh bread was quickly cut with a sharp knife into cubes  $\frac{1}{4}$  inch on a side. These were mixed. One part was taken for immediate test and the other parts were stored, tightly corked, in a special weighing tube.

The tests for the rate of loss of moisture were made in a special weighing tube by which a stream of air or  $\text{CO}_2$  could be drawn through the loosely packed cubes of bread. The loss in weight was considered as moisture (including very small amounts of alcohol and other volatile substances). Air at  $23^\circ \text{C}$ . of 0% and 30% relative humidity was drawn through the bread cubes at rates varying from 18.7 to 119 liters per hour for periods of 7 to 10 hours. The humidity of the air was regulated according to the method of Wilson (1921). The tests were started when the bread was  $2\frac{1}{4}$ , 10, 36, and 60 hours old.

Differences between the rate of loss of moisture of fresh and stale bread treated in the same way were exceedingly small, and showed that this method would not be suitable for measuring the staleness of bread.

Another method attempted was the determination of the rate of loss of moisture by fresh and stale bread when subjected to a vacuum of about 5 mm/Hg. In this case, moisture is lost very rapidly at first and the bread becomes very cold from rapid evaporation. After that, the rate of evaporation is practically controlled by the rate at which heat can be conducted into the bread through the glass of the weighing tube to compensate for heat lost through evaporation. This was evidently, therefore, an unsuitable method

for measuring difference between fresh and stale bread. Curves for weight lost were identical.

### **Tensile Strength**

Bailey (1925) has emphasized the value of physical tests, saying:

"These properties of texture and grain have generally been 'scored' by the baking expert on the basis of observations involving the feeling and appearance of the crumb, a procedure which does not appeal to the scientist, who prefers physical measurement with a suitable instrument. . . . Other physical tests of bread properties are sadly needed in further developing such studies of flour qualities."

In a paper read before the 1923 convention of the American Association of Cereal Chemists, I said (Platt, 1923): "Let us consider the compressibility of a standard cube of bread under a light load, and the elasticity, or the degree to which such cube would recover its normal shape when the load is removed." At that time, I was unaware of the previous work of Katz on the compressibility of bread. I had in mind the already proved usefulness of physical measurements in testing other baked products, such as sweet biscuits, as are described by Davis (1921) and by Platt and Fleming (1923).

Later, I attempted to make some measurements on the tensile strength and compressibility of bread, trying the former first. From a slice of bread one inch thick, I cut with a sharp cutter a piece having the shape of the standard test block of cement. I found it impossible to obtain reliable figures for tensile strength because of uneven tearing, arising from small irregularities in grain.

### **Apparatus for Determination of Compressibility**

In order to determine the compressibility of the crumb of bread, I used the apparatus shown in Figure 1. This is somewhat similar to the one I used in 1914 for testing the jelly-strength of gelatin, and which was described by Oakes and Davis (1922).

The present apparatus is essentially a large balance. Into the underside of the right-hand pan is screwed a plunger (A). Attached to the base of the balance, at a point under the plunger, is a disc (B) for supporting the slice of bread to be tested. This may be elevated or depressed by means of a screw adjustment (C). To



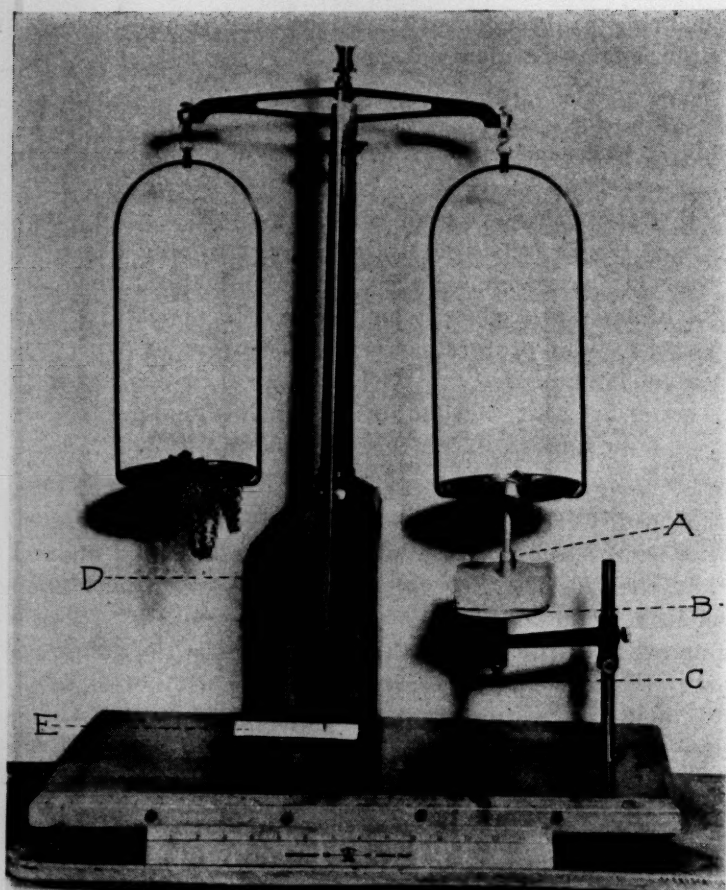


Fig. 1. Apparatus for Measuring the Compressibility of the Crumb of Bread  
Change in compressibility so measured indicates the rate of staling

the beam in the balance is fixed a long pointer (D), the end of which passes in front of a millimeter scale (E). This pointer magnifies the vertical motion of the pans 3.9 times.

### Mode of Operation

Level the balance and see that it swings evenly.

Place a weight, say 250 gm., on the right pan and a chain weighing exactly the same (in this case, 250 gm.) on the left pan so that the pans will still be evenly balanced. Add a small weight to the right pan (5.5 gm. was found convenient.)<sup>2</sup>

<sup>2</sup> Different weights can be used for different types of bread. The same weight would evidently be used in any one series of tests. For the ordinary white pan bread 250 gm. is most convenient. For very soft bread, 150 gm. is convenient.



Cut a slice of bread  $1\frac{1}{2}$  inches thick, trim off the crust, and place the slice on disc B so that the center of the slice comes directly under the plunger.

Place the plunger so that it rests perpendicularly on the center of the slice. The 5.5 gm. extra weight on the right pan will hold the plunger lightly but firmly on the surface of the bread.

Now raise or lower the disc supporting the bread by means of the adjustment screw (C) until the pointer stands at 0 on the scale.

With a slow, regular motion, remove the chain from the left-hand pan, noting the time of removal. This has the effect of *adding* an equivalent weight to the right-hand pan without touching the right-hand pan. Consequently the plunger resting on the bread is not jarred, or pushed sideways.

The reading of the pointer on the scale is taken 60 seconds after the beginning of the removal of the chain. This is recorded as the compressibility of the crumb.

The chain can be removed by hand in a regular, even manner. If desired, this can be accomplished with great uniformity by attaching a thread of negligible weight to the chain. The other end of this thread is attached to a pulley, turning on a separate support placed above the left pan. By turning the pulley at a regular rate, the chain is removed in a very regular manner without jarring.

The slices of bread used for testing should be freshly cut. They should be trimmed so that not only the crust but also the dry, stiff zone immediately below the crust is removed. Slices of the same size should be used throughout any comparative series,  $2\frac{1}{2} \times 2\frac{1}{2}$  inches being a convenient size. Slices are taken throughout the loaf, discarding those within  $1\frac{1}{2}$  inches of the ends of the loaf. In each slice the surface nearest to the center of the loaf is the one upon which the plunger rests. Slices are discarded that show abnormalities such as lumps or large holes where the plunger is to rest. Several loaves are tested from each batch. This averages out the small, accidental, but inevitable differences in texture of different loaves due to differences in molding, proofing and dusting flour, and brings out the differences that are being sought.

### Deviations

Deviations in readings are largest with fresh bread having high penetration. As the bread becomes staler and consequently stiffer, the compressibility becomes less and the readings are much more uniform. The error in tests of the fresher bread can be reduced by increasing the number of slices tested. Rich bread has

larger compressibility and shows larger deviations in readings than leaner bread.

Examination of slices from a considerable number of loaves not only reduces the probable error of the mean and so increases the precision of the results, but also gives an indication of the amount of real variation in any batch of bread. Examination of bread from any batch shows that it not only varies considerably from loaf to loaf but even from slice to slice within the same loaf. These variations are due to lumps formed in the course of manufacture, differences in fermentation, and differences in baking. These differences naturally cause variations in compressibility, swelling power, moisture content, and chemical composition of different sections of the bread. *Any* method for measuring staleness or other characteristics of bread must, therefore, include a considerable number of samples in order to have a basis broad enough to take into consideration the inevitable and important differences always found from slice to slice.

### Advantages

This apparatus and method have the following advantages for measuring the compressibility of the crumb of bread.

1. It is comparatively cheap and generally available, as it can be made from any large balance. If desired, the plunger could be hung from the knife edge at the end of the beam in place of the pan. In this case, the plunger would be loaded with a weight of the desired size.
2. It is smooth in operation, practically frictionless, and without danger of binding.
3. The plunger acts normally to the surface of the bread and there is no disturbing force acting in a tangential direction.
4. The forces may be applied gradually and uniformly in all tests without jarring the plunger or disturbing its position perpendicular to the center of the slice.
5. The apparatus can easily be adjusted to suit different types of bread having widely different compressibility. This is done by varying the diameter of the plunger, which is removable, or the effective weight applied to it.
6. The adjustment of the pointer to zero at the beginning of the test is rapid and accurate. By starting always at zero, for each test, note-taking is simplified and errors of subtraction are eliminated.
7. The crust is trimmed off, so that its effect on the compress-

ibility of the test slice is eliminated. The apparatus determines the compressibility of the crumb only, and is not influenced by the irregular effect of the crust.

8. The apparatus does not require a scientifically trained operator or any elaborate technic to use it satisfactorily.

9. The same apparatus could be used with only minor adjustments for measuring the compressibility and rate of staling of other baked products, such as pound cake and sponge cake.

### Measurement of Rate of Staling

A measurement of the compressibility of the crumb of bread under any given conditions is of value, as is the determination of any other important characteristic, such as loaf volume, which can be measured with known accuracy. By this means, we may check the uniformity of our bread, or compare bread from different factories. By varying any one factor and keeping others constant, we may determine the effect of that factor on compressibility. By introducing such measurable quantities into our system of scoring bread, we may improve the uniformity of our scoring.

Results show a large change in the compressibility of the crumb of bread on aging. This change occurs when the bread is stored under usual commercial conditions, in which loss of moisture is held down to a moderate figure (about 4.7%) and also when it is stored under conditions that prevent any loss of moisture. It is evident that bread of different types will have different compressibility at given age and temperature, so that the compressibility *as such* cannot be used as a measure of staleness.

Inherent staleness, however, may be indicated as the *change* in compressibility, taking as the starting point the compressibility of the crumb as soon after baking as it has reached room temperature, (say 2 hours) and measuring the change in this initial compressibility after a given period of aging.

Also the *rate* of inherent staling over any period in question may be measured by the *rate of change of compressibility* over this period. This may be expressed as the slope of the tangent to the time-compressibility curve.

### Data

Examples of the change in compressibility on aging are shown in Figure 2, also the effect of using different weights. That the bread under these conditions obeys Hooke's Law, namely, that "the strain produced is in proportion to the stress producing it," is

shown in Figure 3. This gives the penetration on the same batch of bread one hour out of the oven when different weights are applied. Pan bread was used in both cases. This was stored unwrapped in a tightly closed chest, formerly an icebox.

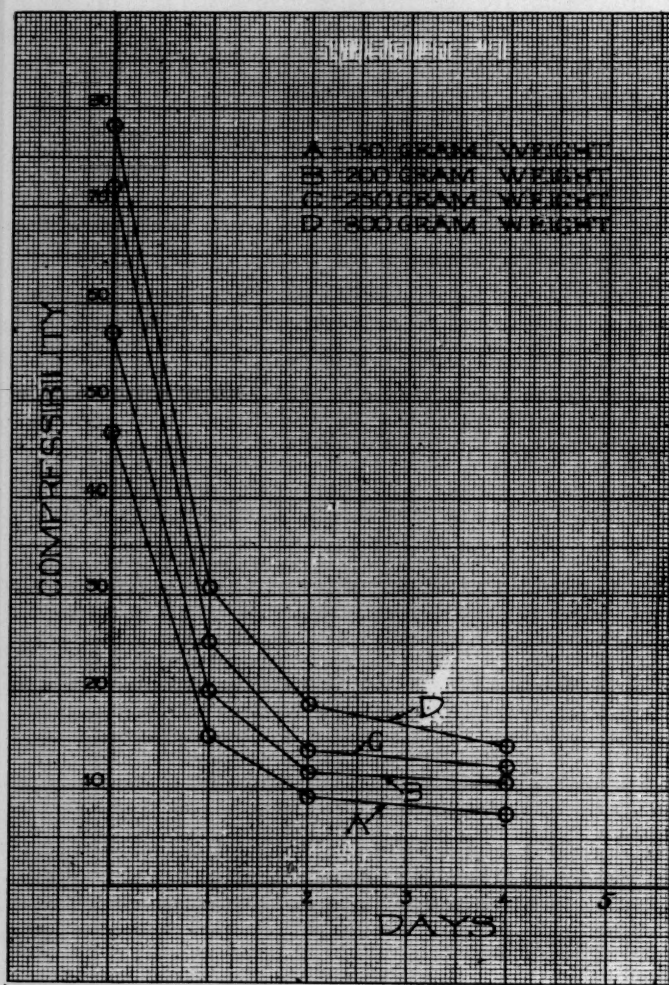


Fig. 2. Effect of Age on Compressibility of Crumb of Bread Using Different Weights Applied to the Plunger

The general effect of temperature on compressibility is shown in Figure 4. In this case, a number of loaves from the same batch were wrapped when  $1\frac{1}{2}$  hours out of the oven and then allowed to stand on an open shelf at room temperature until 16 hours old. The loaves were then divided into three lots. One lot was stored



at 37° C., one lot at room temperature (28° C.) in a closed container, and one at 8° C. All storage was approximately 90% relative humidity. After being stored for four hours, the temperature of the crumb of the bread from these lots was 35°, 28°, and 13° C., respectively.

The bread was sliced and immediately tested for compressibility. A 250-gm. weight was used. Results are given in Figure 4, indicating the influence of temperature on this test.

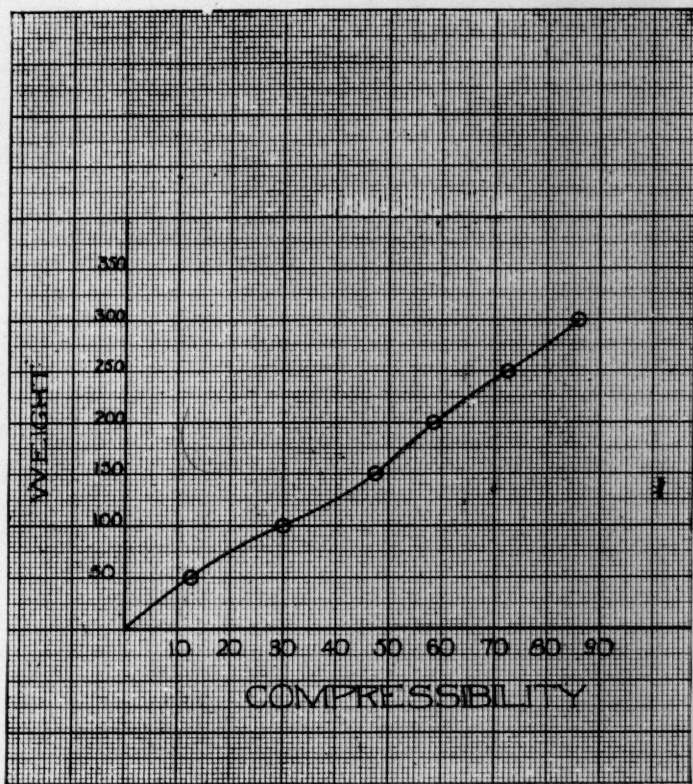


Fig. 3. Effect of Using Different Weights on the Compressibility of Crumb of Bread from the Same Batch when 3 Hours Old

It was possible to increase or decrease the compressibility of the crumb by changing the loaves from cold storage to hot storage or vice versa.

An example of the rate of inherent staling of a soft rich pan bread is shown in Figure 5. This bread is made from a straight dough formula, containing 2.5% dry skimmilk, 3.5% shortening, 0.25% mineral yeast food, and 1.1% yeast.

The bread was wrapped  $1\frac{1}{2}$  hours after leaving the oven and was stored, wrapped, in a tight tin container, which prevented any loss of moisture. Readings were made at  $27^{\circ}\text{C}$ . Table II, from which Figure 5 was drawn, shows the variation in reading to be expected and the size of the probable error.

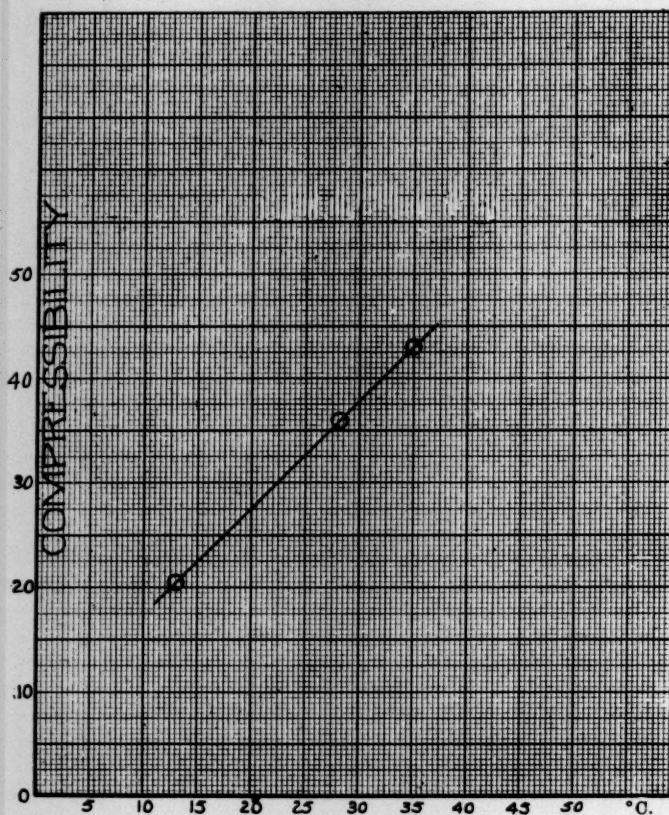


Fig. 4. Effect of Temperature on Compressibility of the Crumb

A single comparison was made between the compressibility and rate of staling of breads made from a lean and a rich formula, both wrapped and unwrapped. This experiment evidently needs to be repeated several times, nevertheless, results are interesting as illustrating the usefulness of the apparatus.

The purpose of the experiment was to apply the instrument to the study of two breads of markedly different composition (rich and lean formulas) in order to obtain data that might show dif-

TABLE II  
COMPRESSIBILITY OF BREAD CRUMB  
Data for Figure 5

	4 hours	6 hours	9 hours	18.5 hours	24 hours	42.3 hours	49.3 hours	60 hours
	39	39	32	15	13	7	5.5	5.5
	34	35	28	13	10.5	7	6	5
	35	35	24	17	10.5	7	6	5
	50	30	27	14.5	9	8	5	6
	42	28	28	11	8	7	6.5	6.5
	41	27	29	13	9	7.5	6	7
	30	31	21	18	10	6	6	5.5
	39	27	23	15	10	7	5	5.5
	42	28	22	16	12	7	6.5	
	35	32	27	15.5	11	6.5	5	
	34	34	28	14	7	7	6	
	30	33	27	18	9	7.5		
			23					
			24					
			23					
Mean	37.6 ± 1.1	31.6 ± .73	25.7 ± .54	15.0 ± .40	10.0 ± .33	7.0 ± .10	5.8 ± .11	5.8 ± .17

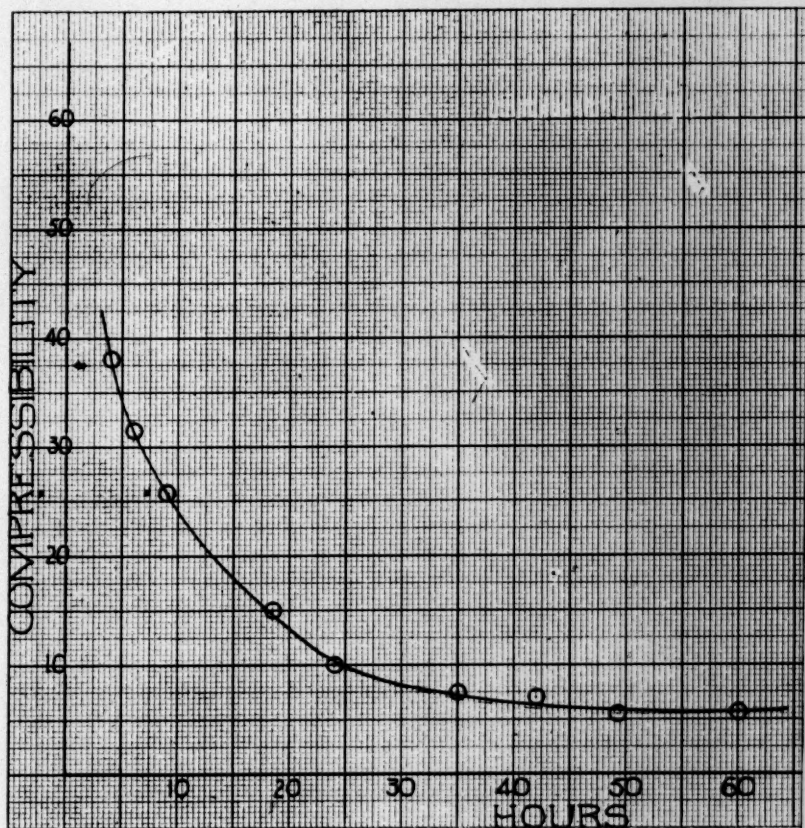


Fig. 5. Effect of Aging on Compressibility of the Crumb of Bread Stored so as to Prevent Loss of Moisture (Data given in Table II)



ferences in keeping quality or staling, based on the compressibility of the crumb. The formulas of Loaf A and Loaf B are as follows:

	Loaf A	Loaf B
Flour, lb. ....	100	100
Water, lb. ....	66	72
Yeast, lb. ....	2	2
Cerelose, lb. ....	1	3
Salt, lb. ....	1.75	2
Shortening, lb. ....	1	3
Malt, lb. ....	0	1.5
Powdered skim milk, lb. ....	0	6
Temperature of mixing, degrees F. ....	80	80
1st punch, min. after mixing. ....	100	95
2nd punch, min. after mixing. ....	145	130
Machine, min. after mixing. ....	166	160
Proofing time, min. ....	70	55
Temperature of proof box, ° F. ....	92	92
Time of baking, min. ....	35	35
Temperature of oven, ° F. ....	360	360
Scaling weight, oz. ....	18	18
Type of pan used, 1 lb. R.T.		

After removing from the oven the bread was allowed to cool for  $1\frac{1}{2}$  hours on a rack in the open room. Half of the total number of loaves were brought unwrapped to the storage room. The rest were wrapped in waxed paper by means of an automatic bread wrapping machine and then transferred to the storage room. The breads to be tested were marked as follows: Loaf A unwrapped, Loaf A wrapped, Loaf B unwrapped, Loaf B wrapped. The storage room was  $6\frac{1}{2} \times 5 \times 6\frac{1}{2}$  feet, with a tightly closed door. After the bread had been out of the oven for one hour several loaves were removed for compressibility tests. These loaves had been stored on the rack in the open room and all were unwrapped.

It is evident that this bread lost some moisture during the aging, the amount of loss being comparable to that which takes place when aging under ordinary commercial conditions.

The relative humidity of the storage room varied from 50 to 70%. The slice of bread  $1\frac{1}{2}$  to 3 inches from the end of the loaf and the center of the surface of the slice 3 inches from the end of the loaf was tested. Two slices from each loaf were tested. At least five loaves were used and the results averaged. Results obtained are shown in Figure 6.

It was surprising to find that the crumb of the wrapped loaves did not show greater differences, as compared with that of the unwrapped loaves. The crust of the wrapped loaves is much softer than that of the unwrapped loaves and when the wrapped and unwrapped loaves are pressed on the outside, one might think that the wrapped loaf is by far the softer on the inside. Altho the



crumb of the wrapped loaves was softer than that of the unwrapped loaves, the difference was not great as measured by the instrument and in the opinion of the judges. The important influence of the crust and of the zone of crumb just under the crust on the feel of the whole loaf is of special interest, as the consumer often judges the freshness of a loaf, by the external feeling, especially at the time of purchase.

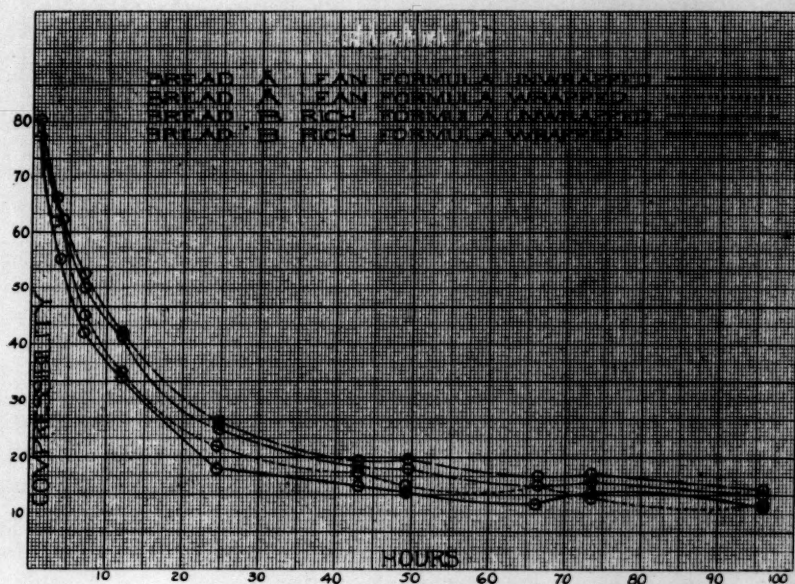


Fig. 6. Typical Compressibility Curves

Loaves from the same batches used in this experiment were judged for keeping qualities by six persons who were unaware of the identity of the loaves being judged. The bread was rated by each judge in the order of decreasing firmness of crumb, giving the firmest, i.e., the stalest, first. Judgment was based on examination with the finger without the use of any apparatus for measurement. Examinations were made when the bread was 24, 43, 72, and 96 hours old.

The judges were by no means unanimous. I have averaged their opinions by assigning a numerical value of 1 to a loaf whenever a judge considered it the stalest, 2 when the loaf was considered second stalest, next 3; and loaves considered least stale, or, in other words, the freshest, were given the value 4. These numerical

ratings by the different judges were then averaged for each age of the bread. Results are shown in Table III.

This table shows:

1. The judgment of judges without instruments coincides with the rating as indicated by the apparatus herein described for actually measuring compressibility of the crumb.
2. The original order of the loaves in regard to staleness remains the same throughout the 96-hour test.
3. Wrapping under these conditions makes less difference in rapidity of staling of the crumb than would have been expected.
4. Influence of formula on rate of staling is unmistakable.

TABLE III  
AVERAGE JUDGMENT OF STALENESS

Figures are average rating of six judges, that with firmest crumb rating 1; second firmest, 2; etc., with freshest rating of 4.

	Average rating			
	24 hr. old	43 hr. old	72 hr. old	96 hr. old
Loaves from lean formula unwrapped	1.0	1.2	1.1	1.5
" " " " wrapped	2.1	2.2	2.1	2.5
" " rich " unwrapped	3.3	2.8	3.0	2.7
" " " " wrapped	3.5	3.8	3.8	3.3

Another experiment was made to determine the difference in rate of staling between breads made from a lean formula and a rich formula, respectively. Bread made according to the formulas just given was used.

In this case, the method was varied by testing the *same loaf* at the beginning and the end of the aging period. To do this, a slice was cut  $1\frac{1}{2}$  to 3 inches from one end of the loaf and tested for compressibility. At the end of the aging period, the corresponding slice from near the other end of the same loaf was tested. This eliminated the variation between loaves, but not the variation between different slices in the same loaf. After the first slice was cut off, the cut end of the loaf was sealed by dipping in melted paraffin, which immediately hardened and prevented loss of moisture from this source. A 250-gm. weight and slices  $2\frac{1}{2}$  inches square were used.

A comparison was made between the bread  $4\frac{1}{2}$  hours and 24 hours old, respectively. Results are given in Figure 7 and in Table IV.

Results show that the bread from the richer formula is softer at the beginning than that made from the lean formula and remains softer, i.e., more compressible, throughout the test; also that the

richer bread has a rate of staling slightly, but significantly, slower than that of the lean bread.

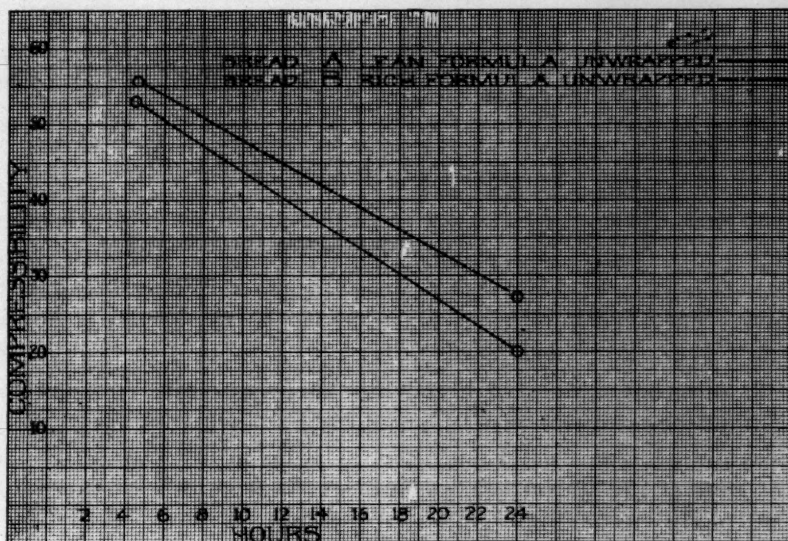


Fig. 7. Comparison of Rate of Staling of Bread Made from Lean and Rich Formulas, as Shown by Compressibility Measurements (Data given in Table IV)

It is planned to continue experiments with the apparatus in order to determine the effect of such ingredients as milk, shortening, and salt on the rate of staling, also the effect of different methods of fermentation and storage.

TABLE IV  
DIFFERENCE IN CHANGE OF COMPRESSIBILITY IN RICH AND LEAN BREAD  
Data for Figure 7

	Lean bread		Rich bread	
	4½ hr. old	24 hr. old	4½ hr. old	24 hr. old
	52.0	19.3	55.8	27.2
	53.5	20.8	47.0	24.5
	51.3	19.8	60.0	25.5
	55.8	20.0	57.0	32.0
	49.0	19.8	52.0	31.3
	56.3	17.7	58.0	24.3
	53.0	20.0	56.3	25.5
	55.0	18.2	53.8	29.3
	41.8*	23.2	56.5	24.5
	51.5	21.0	62.0	26.8
Mean	53.0±.53	20.0±.37	55.8±.9	27.1±.61

Change in compressibility of lean bread over this period is  $53.0 - 20.0 \pm \sqrt{.53^2 + .37^2} = 33.0 \pm .65$

Change in compressibility of rich bread over this period is  $55.8 - 27.1 \pm \sqrt{.9^2 + .61^2} = 28.7 \pm 1.09$

Difference in rate of staling as measured by difference in change in compressibility between lean and rich bread is  $33 - 28.7 \pm \sqrt{.65^2 + 1.1^2} = 4.3 \pm 1.3$

\*Omitted from average as having more than 4 times average deviation calculated without this figure.

This apparatus will give an opportunity for investigators carrying out future experiments like those of Whympers, Berg, Morison, Glabau, and Pirrie, already quoted, involving the keeping quality of bread, to make quantitative determinations on the rate of staling with little additional effort.

### Summary and Conclusions

1. Staling of bread as here considered can be divided into two independent factors, viz, evaporation losses, and inherent staling. The first is easy to understand and to measure by methods already known. The second is less well understood. Oxidation is not important over short periods of storage.

2. Inherent staling of bread has been generally considered to be closely connected with changes in the starch similar to retrogradation, or syneresis. Conditions existing in bread and the characteristics of the staling process indicate that neither of these ideas is adequate to explain inherent staling without considerable modification.

3. The best two methods so far described for measuring the rate of inherent staling are (a) that depending on change of swelling power of the crumb in water, and (b) that depending upon the rate of change of the compressibility of the crumb.

4. An improved apparatus for measuring compressibility is described. This has advantages of availability, ease of operation, and accuracy.

5. It is planned to continue experiments with this apparatus in order to determine by quantitative measurements the effect of various raw materials and methods of manufacture on the rate of inherent staling of bread.

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# RELATION BETWEEN PROTEIN CONTENT AND QUALITY OF WHEAT AS SHOWN BY DIFFERENT BAKING METHODS

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During the course of the last ten years, the use of the protein test to supplement grading of wheat in commercial practice has increased steadily, particularly in the United States and Canada. From this fact it appears evident that the assumption of a close relationship between quantity of protein in the wheat and quality as reflected in baking performance of the flour is justified from the practical standpoint. Despite the faith of the millers in the virtue of the crude protein test, experimenters who have investigated carefully the relation between protein content and quality of wheat have obtained results that at best have to be considered of doubtful practical significance.

Thomas (1917) observed that, in general, strength of flour increases with increasing protein content, except in hard red spring wheat having a crude protein content of over 15 per cent. Stockham (1920) made a similar observation. He found that flour from wheat containing 15 per cent or more crude protein was poor.

The first extensive statistical study of American wheats in regard to the relation between crude protein of wheat and loaf volume of bread appears to have been made by Zinn (1923). Using the published data of the American experiment stations, he found values for the coefficient of correlation between crude protein of wheat and loaf volume ranging from  $+0.7547 \pm 0.0448$  to  $-0.1172 \pm 0.0588$ . Mangels (1926) explained this negative coefficient, so that the range of Zinn's values should perhaps be regarded as  $+0.7547 \pm 0.0448$  to  $+0.1827 \pm 0.0459$ . Blish and Sandstedt (1925), in a study of 112 samples of Nebraska wheats of the crop of 1922, found the correlation coefficient between loaf volume of bread and protein of wheat to be  $+0.304 \pm 0.058$ .

Bailey and Sherwood (1926) obtained a coefficient of correlation of  $+0.271 \pm 0.038$  for loaf volume and protein of flour, using data from tests of 266 samples of hard red spring wheat grown in Minnesota, North Dakota, South Dakota, and Montana.

Mangels (1926) reported values of the coefficient of correlation between protein of flour and loaf volume for eleven crops of North Dakota hard red spring wheat. The values ranged from

$-0.014 \pm 0.049$  to  $+0.547 \pm 0.032$ . For only two crops (1918 and 1924) were the values greater than  $+0.50$ , while two crops (1912 and 1913) showed a slight but not significant negative correlation. He states that "the magnitude of the coefficients of correlation, however, indicates that quantity of protein in flour is not the sole factor which determines the baking strength of the flour," and adds that the diastatic activity of the flour may often be a limiting factor which will affect baking strength. He observes that the correlation coefficient was particularly low for crops produced in dry years, and concludes that "under unusual or unfavorable climatic conditions, gluten quality and diastatic activity may be so reduced that they assume relatively greater importance as quality factors, and the relations existing between protein content and baking quality may be obscured."

Coleman, Dixon, and Fellows (1927) reported the results of an extensive investigation of various physical and chemical means for determining quality of wheat. They concluded that the crude protein determination on either wheat or flour is the best single factor test of gluten quality. The values reported for the correlation coefficient in no case exceeded  $+0.50$ .

With 17 flours obtained from widely separated points, Grewe and Bailey (1927) found a correlation coefficient of  $+0.678 \pm 0.091$  for protein of flour and loaf volume of bread.

Hayes, Immer, and Bailey (1929), in a study of inheritance of quality in diverse strains of spring and winter wheats grown in Minnesota in 1924-27, inclusive, obtained correlation coefficients ranging from  $+0.50 \pm 0.09$  to  $-0.52 \pm 0.12$ . From consideration of the calculated correlation coefficients, they reached the conclusion that with wheats of diverse nature, protein content is not significantly and consistently related to loaf volume.

Table I gives a summary of the results published by these various workers to date.

The correlation between crude protein of wheat or flour and baking quality, altho in most cases significant of a relationship between these two variables, is somewhat too low to justify the application of the protein test as a criterion of flour quality. Despite this, the fact remains that this test seems to be steadily increasing in popularity with manufacturers of bread flours. One might venture to conclude that experimental procedure has failed to confirm entirely commercial experience. As the protein test lends itself to accurate control, the experimental milling and baking technic must be the cause of the lack of agreement.



TABLE I  
CORRELATION BETWEEN PROTEIN OF WHEAT OR OF FLOUR AND LOAF VOLUME,  
AS REPORTED BY VARIOUS WORKERS

Author	Material studied	No. of samples	Correlation coefficient	Probable error	
Zinn (1923)	Flour from commercial varieties:				
	North Dakota spring wheat	119	— 0.0987	± 0.0612	
	Minnesota " "	203	+ .2586	± .0442	
	Montana " "	34	+ .3448	± .1019	
	Colorado " "	48	+ .6130	± .0608	
	Minnesota winter wheat	43	+ .6496	± .0594	
	Montana " "	91	+ .3620	± .0614	
	Kansas " "	43	+ .7956	± .0377	
	Ohio " "	99	+ .4709	± .0528	
	Pure strains				
	North Dakota spring wheat	28	+ .3018	± .1158	
	Minnesota " "	48	+ .5469	± .0689	
	Ontario " "	16	+ .5752	± .1129	
	Wisconsin winter wheat	25	+ .3990	± .1134	
	Ohio " "	25	+ .5560	± .0932	
	Wheat of commercial varieties				
	North Dakota spring wheat	128	— .1172	± .0588	
	Minnesota " "	202	+ .1827	± .0459	
	Montana " "	34	+ .3555	± .1011	
	Colorado " "	48	+ .4908	± .0739	
	Montana winter wheat	91	+ .3638	± .0613	
	Ohio " "	100	+ .5394	± .0479	
	Minnesota " "	43	+ .5874	± .0674	
	Kansas " "	42	+ .7547	± .0448	
	Pure strains				
	Minnesota spring wheat	48	+ .4621	± .0766	
	Wisconsin " "	22	+ .5123	± .1061	
	Maine " "	31	+ .5194	± .0885	
	Ohio winter wheat	25	+ .5548	± .0934	
	Mangels (1926)	North Dakota hard red spring wheat flour	1912	72	— .064
" " "		1913	186	— .014	± .049
" " "		1914	123	+ .312	± .055
" " "		1915	172	+ .384	± .044
" " "		1916	212	+ .473	± .036
" " "		1917	197	+ .187	± .046
" " "		1918	217	+ .547	± .032
" " "		1921	128	+ .307	± .053
" " "		1922	136	+ .427	± .047
" " "		1923	194	+ .345	± .043
" " "		1924	170	+ .508	± .038
Grewe and Bailey (1927)		Various flours	17	+ .678	± .091
Bailey and Sherwood (1926)		Commercial samples, 1921-25*	266	+ .271	± .038
Blish and Sandstedt (1925)	Nebraska Wheat	1922	112	+ .304	± .058
Coleman, Dixon, and Fellows (1927)	Commercial Samples				
	Hard red spring wheat	1923	128	+ .4610	± .0470
	" " winter "	1923	183	+ .4281	± .0407
	Pure varieties				
	Hard red spring wheat	1924	116	+ .4184	± .0517
	" " winter "	1924	76	— .0370	± .0773
Hayes, Immer, and Bailey (1929)	Pure varieties and strains				
	Spring wheat	1924	26	+ .31	± .12
	" " "	1925	34	+ .50	± .09
	" " "	1926	34	+ .17	± .11
	" " "	1927	24	+ .07	± .14
	Winter wheat	1925	18	+ .11	± .16
	" " "	1926	18	— .52	± .12

\* Including all hard red spring wheat flour (Minn., N. D., S. D., and Mont.)

It was pointed out by Larmour and MacLeod (1929) that experimentally milled flour from wheat of high protein content, when baked by the basic formula—flour, yeast, sugar, salt, and water only—in many instances gives results entirely out of agreement with the known commercial value of the wheat. They concluded that a bromate formula containing, in addition to the above mentioned ingredients, 0.001%  $\text{KBrO}_3$ , gives results that are a better measure of quality.

The response of experimentally milled flours to  $\text{KBrO}_3$  varies from year to year. In 1926 the wheat produced in Saskatchewan was high in protein content, and in most cases baking results by the basic procedure were low. This is in agreement with the observations made by Thomas (1917) and Stockham (1920) to the effect that flour from wheat of over 15 per cent protein was poor in baking quality. When, however, these flours were baked with the addition of 0.001%  $\text{KBrO}_3$ , a remarkable stimulation occurred, and bread of most excellent volume and quality was produced. In 1927 the protein content of our pure Marquis samples averaged nearly 10% lower than that of the 1926 crop, and the values obtained by the basic formula were much higher. The response to  $\text{KBrO}_3$  however was less. The 1928 samples differ in this respect from either of the two previous crops as the flours in general show a rather high value by the basic formula and still respond notably to  $\text{KBrO}_3$ .

Larmour and MacLeod (1929a) have shown that the baking value of flours obtained by use of the formula including  $\text{KBrO}_3$  agrees fairly well with the ability of the corresponding flours to stand up in a blend with very low strength flour; the basic formula gives no accurate measure of this property. It seems likely, therefore, that the baking values obtained by the bromate formula give a measure of quality that is much more reliable than the values obtained by the basic formula, and are more significant for use in studying the relation of crude protein of wheat to baking quality of flour. This paper deals with estimates of the correlation between crude protein of wheat and quality of flour as expressed in both loaf volume alone and in the computed baking score.<sup>1</sup>

<sup>1</sup> Computed baking score is calculated as follows:

Loaf volume (cc. minus 400).....	x 0.2
Absorption (% minus 60).....	x 1
Texture (including grain and texture) x 3	
Crumb color .....	x 2
Outer appearance .....	x 1
Total = Computed baking score	

For details of method of scoring see Larmour and MacLeod, *Sci. Agr.* 9: 477-490 (April, 1929).

Zinn (1923) expressed the opinion that the proper approach to the solution of the question of correlation between various characters of wheat and flour must be based upon many data secured from analyses of pure lines and made by the same laboratory, rather than on analyses of commercial varieties. In dealing with commercial samples, varietal differences and the effect of environment under which the grain was grown are largely unknown factors, and it is difficult to estimate what effect, if any, these factors may have upon the results obtained. All the data dealt with in this study were obtained on samples of pure varieties. Many of these samples were grown in a given year from the same lot of pure seed, and in such material varietal differences may be considered reduced to the minimum. To avoid errors attributable to various sorts of damage, the results on wheat of grades 1, 2, and 3 Northern have been grouped for the most part, and these data are considered the most conclusive. Some studies were made in which the samples were grouped by varieties.

All the samples were baked by both the basic and the bromate formulas. The former involves the use of flour, water, yeast, salt, and sugar only; the latter has, in addition, 0.001%  $\text{KBrO}_3$ . In addition to the basic and bromate baking formulas, a third was used on all 1928 samples. This was a blend formula similar to the bromate formula, except that in place of 100 grams of the flour being tested, a blend consisting of 60 per cent of the flour under observation and 40 per cent of a Pacific White Club wheat flour was used. The procedure was strictly fixed and the same for all bakings. Calculations have been made using both loaf volume and the computed baking score as measures of the baking quality.

Table II shows calculated correlation coefficients for protein of wheat and baking quality of pure samples of Marquis grown in the years 1926, 1927, and 1928. Probable error was calculated in all cases by the formula

$$\text{P.E.} = \frac{0.6745 (1-r^2)}{(n)^{\frac{1}{2}}}$$

When the samples were few, the value  $t$  was calculated from the formula given by Fisher (1928),

$$t = \frac{r (n' - 2)^{\frac{1}{2}}}{(1 - r^2)^{\frac{1}{2}}}$$

where  $n'$  equals the number of samples. Approximate values of  $P$ , the probability of occurrence of such a value of  $r$  by random

sampling from an uncorrelated population were obtained from Table IV, p. 139, Fisher (1928).

The 1926 samples, Group A, were all grown in various districts of Saskatchewan from the same lot of seed. In 1927 two strains of Marquis were used—Marquis 10b and Ottawa 15. The data from these have been considered separately in Groups B and C and

TABLE II  
CORRELATION BETWEEN CRUDE PROTEIN OF WHEAT AND BAKING QUALITY AS  
DETERMINED BY VARIOUS BAKING METHODS  
Pure Marquis grown on plots in various localities in Saskatchewan.

Group	Baking Formula	Year	No. of samples	Correlation coefficient	Probable error	$r_{xy}$ P.E.	t	P
A	Basic — Loaf volume	1926	24	-0.0018	±0.138	0.013	0.008	>0.9
	" C.B.S.*	"	"	-.222	±.131	1.7	1.068	.3
	Bromate—Loaf volume	"	"	+.518	±.101	5.1	2.840	<.01
B	" C.B.S.	"	"	+.552	±.096	5.8	3.105	<.01
	Basic — Loaf volume	1927	15	-.157	±.170	0.9	0.573	>.5 <.6
	" C.B.S.	"	"	-.288	±.160	1.8	1.084	0.3
C	Bromate—Loaf volume	"	"	+.557	±.120	4.6	2.418	>.02 <.05
	" C.B.S.	"	"	+.497	±.131	3.8	2.065	>.05 <.1
	Basic — Loaf volume	"	12	+.668	±.108	6.2	2.838	<.02
D	" C.B.S.	"	"	+.666	±.108	6.2	2.824	<.02
	Bromate—Loaf volume	"	"	+.405	±.163	2.5	1.401	<.2
	" C.B.S.	"	"	+.450	±.155	2.9	1.593	>.1 <.2
E	Basic — Loaf volume	"	27	+.108	±.128	0.8	0.543	>.5
	" C.B.S.	"	"	+.001	±.130	0.01	0.005	>.9
	Bromate—Loaf volume	"	"	+.478	±.100	4.8	2.721	.01
F	" C.B.S.	"	"	+.470	±.101	4.6	2.662	.015
	Basic — Loaf volume	"	60	+.530	±.063	8.5		
	" C.B.S.	"	"	+.534	±.062	8.6		
G	Bromate—Loaf volume	"	"	+.678	±.047	14		
	" C.B.S.	"	"	+.709	±.043	16		
	Basic — Loaf volume	1928	12	+.453	±.155	2.9	1.607	>.1 <.2
H	" C.B.S.	"	"	+.041	±.194	0.2	0.130	0.9
	Bromate—Loaf volume	"	"	+.919	±.030	30	7.372	<.01
	" C.B.S.	"	"	+.716	±.095	7.5	3.243	<.01
I	Blend — Loaf volume	"	"	+.902	±.036	25	6.607	<.01
	" C.B.S.	"	"	+.879	±.044	20	5.829	<.01
	Basic — Loaf volume	"	22	+.410	±.120	3.4	2.010	.05
J	" C.B.S.	"	"	+.137	±.141	1	0.619	>.5 <.6
	Bromate—Loaf volume	"	"	+.878	±.033	27	8.204	<.01
	" C.B.S.	"	"	+.799	±.052	15	5.942	<.01
K	Blend — Loaf volume	"	"	+.796	±.053	15	5.881	<.01
	" C.B.S.	"	"	+0.679	±0.077	9	4.136	<0.01

\*Computed Baking Score.

combined in Group D. Group E is comprised of 60 samples of Marquis, Saskatchewan 7, all grown on the University Farm. The 1928 samples were grown from the same lot of Marquis, 10b. Owing to frost, only 12 of the 37 samples grown graded 3 Northern or higher. Data on these have been considered in Group F. Ten of the remaining samples, altho grading No. 4 and No. 5, gave no evidence of injury from frost, in either milling value or baking quality. The data on these were combined with those of Group F



to form Group G of 22 samples. These groups are being discussed first because the material is thought to be free of such disturbing unknown factors as damage and differences in variety.

Considering the values of the correlation coefficient obtained by using the loaf volume and computed baking score respectively, the latter expression of baking quality generally gives the lower result. In computing a single figure estimate for baking quality the loaf volume is subjected to discounts for texture, color, appearance, and absorption when these happen to fall below a normal value. From *a priori* reasoning, such discounting might be expected to raise, lower, or leave unaltered the correlation with protein content of wheat. In the groups of samples discussed in this paper the three cases have occurred, but in general there seems to be a tendency for lower correlation coefficients with the single-figure estimate than with loaf volume. Not enough cases have been studied to enable one to state that this is generally true. Larmour (1929) has given reasons for considering the computed baking score a better general estimate of quality than loaf volume alone, and in this paper the correlation between baking quality and protein of wheat will be judged from the value of the correlation coefficient obtained by this single-figure estimate.

With the groups of Table II heretofore described, in all except one case, Group C, the data with the basic formula yielded lower values of the correlation coefficient than those with the bromate formula. In Groups A and B, the basic data showed small and not significant negative correlation; the bromate data showed values of  $+0.552 \pm 0.096$  and  $+0.497 \pm 0.131$ , respectively, indicating a marked correlation. Group C, representing the 1927 samples of Marquis, Ottawa 15, presents one of the two cases observed in which the correlation coefficient is higher for the basic data than for the bromate data.

Group D, a combination of Groups B and C, shows no significant correlation for the basic data and a significant but somewhat low correlation for the bromate data.

Group E is unique and particularly interesting for a study such as this. The 60 samples, obtained through the courtesy of Professor Champlin, of the Field Husbandry Department, University of Saskatchewan, were produced in a rotation experiment. They were grown from the same lot of pure Marquis, Saskatchewan 7 seed, on an area of approximately 20 acres. It may be safely assumed, therefore, that all influencing factors except soil were constant.

The protein content varied between 9.0 and 14.0%. The samples were not graded commercially, but there is little doubt that they were all 3 Northern or higher. As seed they graded 2 Northern, being discounted for a slight amount of bleaching. The basic data gave a marked positive correlation,  $+0.534 \pm 0.062$ ; the bromate data showed a higher correlation,  $+0.709 \pm 0.043$ .

The 1928 samples of Marquis represented in Groups F and G give low and not significant positive correlation coefficients for the basic data; the bromate and blend data give high significant positive values.

Table III gives calculations of the correlation coefficient for three small groups, the samples in each of which were grown in various localities of Saskatchewan from the same lot of pure seed.

TABLE III  
CORRELATION BETWEEN CRUDE PROTEIN OF WHEAT AND BAKING QUALITY  
AS DETERMINED BY VARIOUS BAKING METHODS  
Pure samples of Garnet and Kota grown on plots in various localities in Saskatchewan.

Group	Baking formula	No. of samples	Correlation coefficient	Probable error	$r_{xy}$ P.E.	t	P	
KOTA — 1927								
A	Basic — Loaf volume	12	+0.623	±0.119	5.2	2.519	>0.02	<0.05
	" C.B.S.		+ .608	± .123	5.0	2.422	< .05	
	Bromate—Loaf volume		+ .629	± .118	5.3	2.559	> .02	< .05
	" C.B.S.		+ .524	± .141	3.7	1.945	> .05	< .1
GARNET — 1927								
B	Basic — Loaf volume	10	+ .469	± .130	3.6	1.502	> .1	< .2
	" C.B.S.		+ .566	± .145	3.9	1.941	> .05	< .1
	Bromate—Loaf volume		+ .719	± .103	7.0	2.926	> .02	
	" C.B.S.		+ .740	± .096	7.7	3.112	> .01	< .02
GARNET — 1928								
C	Basic — Loaf volume	13	+ .453	± .149	3.0	1.685	> .1	< .2
	" C.B.S.		+ .235	± .177	1.3	0.802	> .4	< .5
	Bromate—Loaf volume		+ .872	± .045	19	5.908	< .01	
	" C.B.S.		+ .784	± .072	11	4.189	< .01	
	Blend — Loaf volume		+ .502	± .140	3.6	1.925	< .1	
	" C.B.S.		+ 0.528	± 0.135	3.9	2.062	< 0.1	

Two of the 12 samples of Kota in Group A graded 4 C. W. owing to thinness of kernel; the rest graded 3 C. W. or higher. In Group B, one sample of No. 4 was included, the rest being 3 Northern or higher. In Group C all samples were 3 Northern or higher.

Few samples were used in these groups and the results are not very conclusive. In Group A the correlation coefficient for basic computed baking score is higher than the corresponding bromate value. Group B presents one of the few cases in which the correlation of protein with computed baking score is higher than with loaf volume. In Group C the correlation of protein with

the basic and blend data is low and not significant; with the bromate data it is high.

In Table IV are shown correlation coefficients obtained with samples of hard red spring wheat procured from the exhibits of the 1928 provincial seed fair of Saskatchewan. These samples are

TABLE IV  
CORRELATION BETWEEN CRUDE PROTEIN OF WHEAT AND BAKING QUALITY  
AS DETERMINED BY VARIOUS BAKING METHODS  
Pure varieties from the Saskatchewan Seed Fair exhibits of 1928.

Group	Baking formula	No. of samples	Correlation coefficient	Probable error	$r_{xy}$ P.E.	t	P
MARQUIS							
A	Basic — Loaf volume	38	+0.451	±0.087	5		
	" C.B.S.		+ .079	± .109	0.07		
	Bromate—Loaf volume		+ .852	± .030	28		
	" C.B.S.		+ .801	± .039	20		
	Blend — Loaf volume		+ .758	± .046	16		
	" C.B.S.		+ .719	± .053	14		
GARNET							
B	Basic — Loaf volume	16	+ .876	± .039	22	6.796	<0.01
	" C.B.S.		+ .780	± .066	12	4.664	< .01
	Bromate—Loaf volume		+ .785	± .065	12	4.741	< .01
	" C.B.S.		+ .730	± .079	9	3.997	< .01
	Blend — Loaf volume		+ .516	± .124	4	2.254	< .05
	" C.B.S.		+ .483	± .129	3.7	2.064	< .05
REWARD							
C	Basic — Loaf volume	13	+ .689	± .098	7	3.153	.01
	" C.B.S.		+ .551	± .130	4	2.190	.05
	Bromate—Loaf volume		+ .917	± .030	31	7.624	< .01
	" C.B.S.		+ .920	± .029	32	7.786	< .01
	Blend — Loaf volume		+ .825	± .060	14	4.842	< .01
	" C.B.S.		+ .492	± .142	3.5	1.874	0.1
TOTAL, MARQUIS, GARNET, AND REWARD							
D	Basic — Loaf volume	67	+ .762	± .035	22		
	" C.B.S.		+ .620	± .051	12		
	Bromate—Loaf volume		+ .916	± .013	69		
	" C.B.S.		+ .865	± .021	42		
	Blend — Loaf volume		+ .759	± .035	22		
	" C.B.S.		+ .695	± .043	16		
MARQUIS AND REWARD							
E	Basic — Loaf volume	51	+ .691	± .049	14		
	" C.B.S.		+ .490	± .072	7		
	Bromate—Loaf volume		+ .909	± .016	55		
	" C.B.S.		+ .880	± .021	41		
	Blend — Loaf volume		+ .714	± .046	15		
	" C.B.S.		+0.611	±0.088	7		

excellent material for a study such as this, because none graded lower than 2 Northern and they were practically free from damage. They were grown in widely scattered districts of the province, and fairly represent the best wheat of the season. They have been studied according to variety and as a whole.

The high values of the correlation coefficient obtained by using the data of the bromate formula leave no doubt of the significance of the relation of protein and baking quality as determined by this

method. The low values obtained with the blend data for Group B are somewhat difficult to explain. Similar results were obtained with the Garnet samples of Group C, Table III.

The low value of the correlation between protein and baking score of the Reward blend in Group C is largely due to one of the samples, which was scored down severely on account of color. When this is omitted, the value of  $r$  becomes  $+0.635 \pm 0.116$ .

Table V gives the correlation coefficients for all the 1928 data on samples grading 3 Northern or higher. The values of  $r$  with the basic, bromate, and blend baking scores are  $+0.416 \pm 0.043$ ,  $+0.814 \pm 0.018$ , and  $+0.763 \pm 0.022$ , respectively.

TABLE V  
CORRELATION BETWEEN CRUDE PROTEIN OF WHEAT AND BAKING QUALITY  
AS DETERMINED BY VARIOUS BAKING METHODS  
Pure varieties grading 3 Northern or higher, grown in 1928.

Baking formula	No. of samples	Correlation coefficient	Probable error	$r_{xy}$ P.E.
Basic — Loaf volume	164	+0.619	$\pm 0.032$	19
"      C.B.S.		+ .416	$\pm .043$	9
Bromate—Loaf volume		+ .871	$\pm .013$	69
"      C.B.S.		+ .814	$\pm .018$	46
Blend — Loaf volume		+ .801	$\pm .019$	42
"      C.B.S.		+0.763	$\pm 0.022$	35

Table VI gives the values of  $r$  obtained with all the data procured in the years 1926, 1927, and 1928 on pure line samples grading 3 Northern or higher. The material used may be described briefly as follows:

Year	Variety	No. of samples
1926 .....	Marquis .....	24
Total for 1926 .....		24
1927 .....	Marquis .....	80
	Garnet .....	9
	Kota .....	9
Total for 1927 .....		98
1928 .....	Marquis .....	74
	Garnet .....	35
	Reward .....	25
	Other varieties .....	30
Total for 1928.....		164

TABLE VI  
CORRELATION BETWEEN CRUDE PROTEIN OF WHEAT AND BAKING QUALITY  
AS DETERMINED BY VARIOUS BAKING METHODS  
Pure varieties grading 3 Northern or higher, grown in 1926, 1927 and 1928.

Baking formula	No. of samples	Correlation coefficient	Probable error	$r_{xy}$ P.E.
Basic — Loaf volume	286	+0.280	$\pm 0.037$	7
"      C.B.S.		+0.134	$\pm 0.040$	3.4
Bromate—Loaf volume		+0.711	$\pm 0.020$	36
"      C.B.S.		+0.667	$\pm 0.022$	30



The "other varieties" included samples of Red Fife, Kitchener, Red Bobs, Renfrew, Producer, Kota, and Ceres. The correlation coefficients for protein of wheat and computed baking scores, using 286 pure-line samples of various hard red spring wheats were  $+0.134 \pm 0.040$  and  $+0.667 \pm 0.022$  for the basic and bromate data, respectively. Values of  $r$ , using loaf volume were slightly higher in each case.

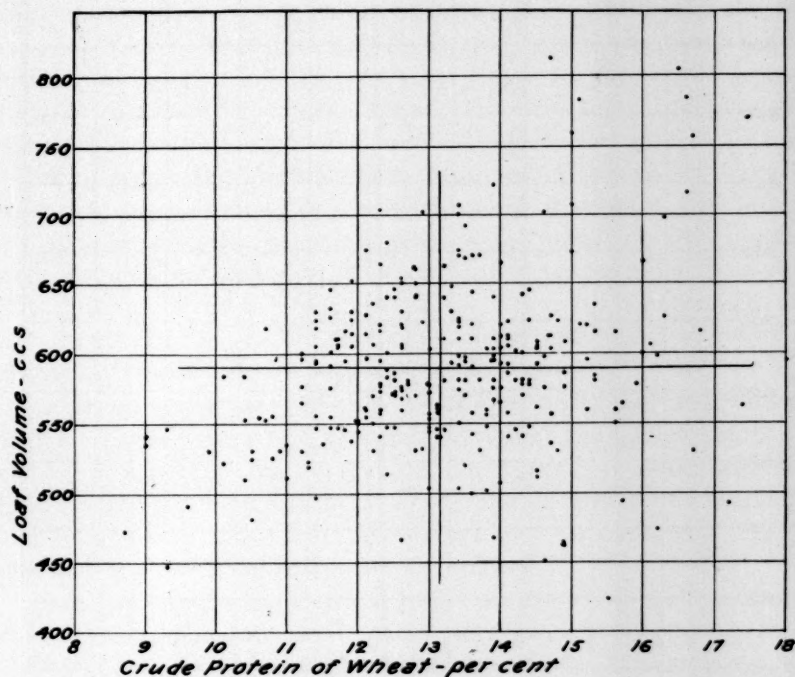


Fig. 1. Protein of Wheat and Loaf Volume (Basic Formula)  
Pure varieties of contract grades grown in 1926, 1927, and 1928.  
 $n = 286$ ,  $r = +0.280 \pm 0.037$

Figure 1 is a dot diagram of the basic loaf volume and protein data for the 286 samples of Table VI; Figure 2 is a dot diagram for the bromate loaf volume and protein data. These figures are included to give a concrete representation of the practical significance of the correlation coefficient. In Figure 1 loaf volume and protein give a value  $r = +0.280 \pm 0.037$ . As a statistic this figure is highly significant, but from the practical standpoint so small a degree of correlation of these variates has little significance.

For the data represented in Figure 2,  $r = +0.711 \pm 0.020$ . As correlation coefficients go, this is a high value and there is no doubt

of its significance as a statistic. Moreover, it indicates a fairly high probability of predicting loaf volume from protein. Yet even with such a high correlation, it can be seen from the scatter diagram that the chances for error are very large indeed. It seems that before being considered significant in a practical sense, the correlation as expressed by  $r$  should be quite high.

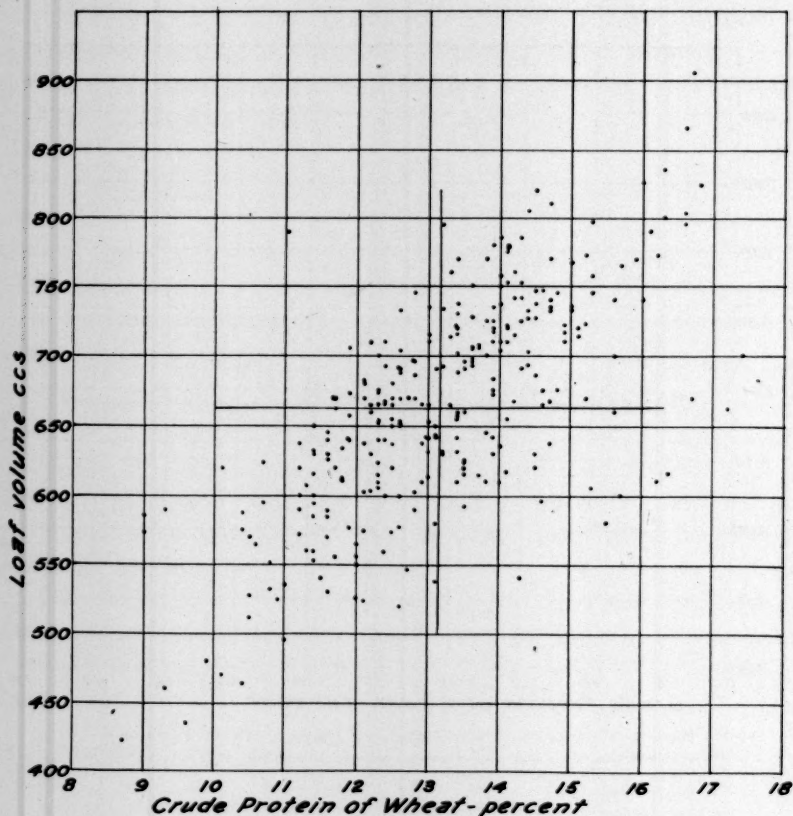


Fig. 2. Protein of Wheat and Loaf Volume (Bromate Formula)  
Pure varieties of contract grades grown in 1926, 1927, and 1928.  
 $n = 286$ ,  $r = +0.711 \pm 0.020$

The data have demonstrated a significant positive correlation between protein content and quality of wheat. This, however, was not the sole purpose of these studies. Different methods have been used for determining a value for the term "quality of wheat" and the results obtained show varying degrees of correlation with the protein content. It is realized that the values of  $r$  for the respective methods cannot be used to judge their merits. There are,

however, facts in connection with the problem that, when considered together, may justify drawing certain inferences. The most important fact is that after nearly 10 years of experience with the crude protein test as an estimate of the quality of wheat, millers in America continue to use it. It might be concluded that practical experience has demonstrated the existence of a correlation between protein and quality sufficiently high to justify the cost of determining crude protein. Commercial usage does not constitute proof, but it provides good circumstantial evidence. On the other hand, as was pointed out earlier in this paper, the results of experimental milling and baking tests have on the whole failed to show a correlation between these two varieties high enough to justify the present extensive application of the protein test as a factor in predicting quality. Data reported in this paper show that baking results obtained by the basic method usually give low values of the correlation coefficient with protein. Other baking methods, and particularly the Werner bromate formula, give values that show a correlation with protein content high enough to warrant the use of the protein test as an important factor in evaluating quality of sound hard red spring wheat.

Assuming the basic baking procedure to be the best, one may infer from the values of  $r$  reported here that the use of the protein test is of doubtful practical value. On the other hand, admitting the bromate procedure to be a more reliable means for estimating quality, one may infer from the values of  $r$  obtained that the protein test is a fairly useful index of quality.

Our experience leads to the inference that the basic procedure, when used as the sole method for determining baking quality, is unreliable; the bromate method yields results that correspond fairly consistently with well established commercial valuations.

### Summary

A study was made of 286 samples of pure varieties, mostly Marquis, grown in Saskatchewan in 1926, 1927, and 1928. They were milled in an experimental mill and the flours were baked by a simple formula of flour, water, salt, yeast, and sugar, and also by a formula including  $KBrO_3$ . In the author's opinion the latter method gives a more accurate measure of quality than the former. Correlation coefficients for protein of wheat and quality, as measured by the bromate method, were in practically all cases sufficiently high to warrant concluding that the relation between these two characters of sound wheat is significant enough to justify the

commercial use of the protein test as a factor in the classification of hard red spring wheat.

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# **BUFFER INTENSITIES OF WATER EXTRACTS AND SUSPENSIONS OF VARIOUS FLOURS AT DIFFERENT H-ION CONCENTRATIONS**

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Jessen-Hansen (1911) and Cohn and Henderson (1918) pointed out that conditions for fermentation are at optimum when a H-ion concentration represented by a pH of approximately 5.00 is reached.

Jessen-Hansen also pointed out that the lower grades of flour have a greater buffer capacity than do the higher grades.

Bailey and Peterson (1921) determined the changes in H-ion concentration of water extracts of different grades of spring wheat flours, with addition of acid and alkali, over a wide range. From this titration the senior author (1925) subsequently calculated the average buffer index of each flour for the entire range of H-ion concentration used, and pointed out the correlation of these values with the ash content of the flours.

The buffer action of an extract of a flour is, however, not identical with that of its water suspension, as a water extract does not contain all the buffer substances of the flour. Titration curves upon the extracts therefore do not represent correctly the resistance offered by various flour doughs to changes in H-ion concentration during the addition or development of acid.

## **Experimental**

Preparatory to some fermentation studies it was desired to know to what extent flours of different types exerted a buffer action in the various ranges of H-ion concentration. For these experiments four grades each of hard winter wheat and soft winter wheat flours were chosen. The ash content of these flours and of four hard spring wheat flours used by Bailey and Peterson, the data of which are used in subsequent calculations, are given in Table I.

Twenty-gram samples of each of the flours were suspended in 100 cc. of water. Varying amounts of 0.20 N alkali and acid were added to each of the suspensions, which were then allowed to stand for 3 hours with occasional stirring, at which time the H-ion con-

TABLE I  
ASH CONTENT OF GRADES OF FLOUR OF VARIOUS TYPES

HARD SPRING WHEAT FLOUR *	
Flour grade	Ash content %
Patent	0.40
5th middlings	0.61
4th middlings	1.17
2nd break	2.38
HARD WINTER WHEAT FLOUR	
Patent	0.36
Low grade	0.63
Sizing	0.97
2nd break	2.30
SOFT WINTER WHEAT FLOUR	
Patent	0.33
3rd grind	0.67
4th middlings	1.32
2nd break	2.35

\*From data of Bailey and Peterson.

centration was determined upon the supernatant liquid removed from each suspension.

Preliminary determinations of the H-ion concentration of several of the samples with both the hydrogen and the quinhydrone electrodes indicated that the agreement between results obtained was good with samples to which acid had been added. With those samples to which more than 2 cc. of 0.20 N alkali had been added, the deviation in the results was marked, especially those obtained upon samples of low ash content. With several of the samples considerable difficulty was experienced in obtaining saturation of the hydrogen electrode, when working in the alkali range.

TABLE II  
H-ION CONCENTRATION, AS pH, OF VARIOUS SUSPENSIONS OF A SOFT WHEAT FLOUR

0.20 N acid added	0.20 N alkali added	Hydrogen electrode	Quinhydrone electrode	Difference between quinhydrone and hydrogen electrode
cc.	cc.	pH	pH	pH
	5	8.88	8.44	-0.44
	4	7.96	7.86	-.10
	3	7.38	7.47	.09
	2	6.86	6.94	.08
	1	6.62	6.62	.00
0	0	6.32	6.37	.05
1	.....	6.15	6.19	.04
2	.....	5.94	5.98	.04
3	.....	5.78	5.78	.00
4	.....	5.52	5.55	.03
5	.....	5.25	5.28	.03
6	.....	5.06	5.11	.05
7	.....	4.73	4.74	.01
8	.....	4.54	4.58	.04
9	.....	4.22	4.26	.04
10	.....	3.52	3.56	0.04

Table II gives the correlation between the values obtained by the two methods upon a soft wheat flour of 1.32 per cent ash content.

As already stated, the deviations of the results obtained by the two methods in the alkaline range were in most cases greater than those shown for this sample. In the work reported, therefore, the H-ion concentration determinations upon the check and those to

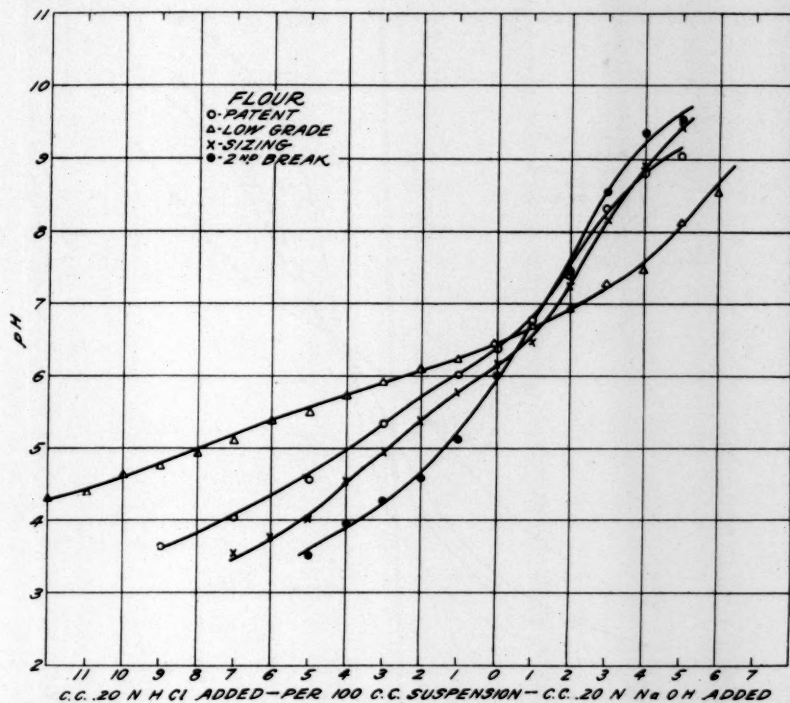


Fig. 1. Titration Data upon Hard Winter Wheat Flour Suspensions

which alkali had been added were determined with the hydrogen electrode, while where acid had been added the quinhydrone electrode was used.

Titration were similarly carried out upon the water extracts of these flours. These extracts were prepared by suspending 100 grams of flour in 500 cc. of water and allowing the suspension to stand for three hours at 26° C. with occasional stirring. The suspended matter was centrifuged out and aliquots of the supernatant liquid were used in the titrations.

### Titration Data

**Hard winter wheat flour**—The data shown in Figure 1 were obtained upon the various samples of a hard winter wheat flour suspension; those in Figure 2 were obtained with extracts of the same samples.

The data indicate clearly that the buffer capacity of the flour suspension is greater than that of the extract.

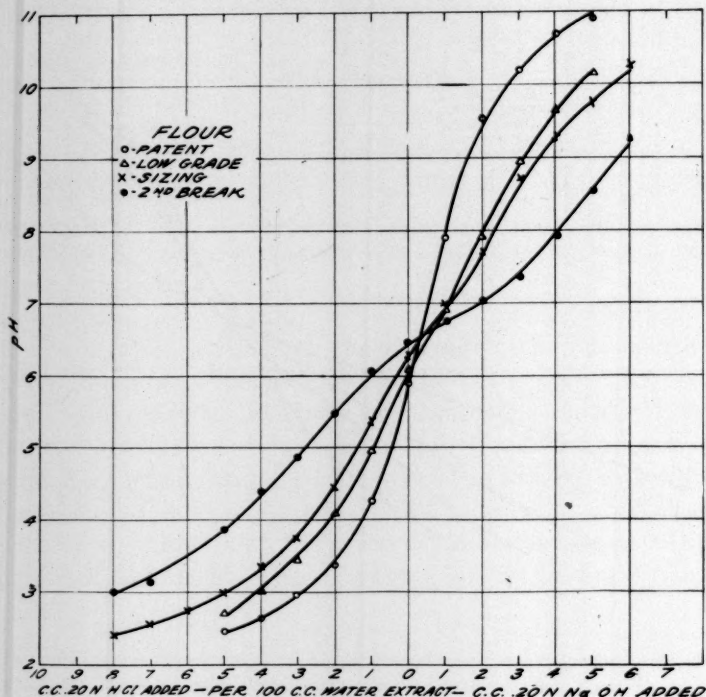


Fig. 2. Titration Data upon the Water Extracts of Hard Winter Wheat Flours

**Soft spring wheat flour**—The titration data for the samples of this flour are recorded in Figures 3 and 4.

Likewise, in Figures 4 and 5 the greater buffer capacity of the suspensions is evident.

### Buffer Intensities

Although titration data show the relative buffer effects over the range of titration, they do not indicate clearly or in a quantitative manner the relative buffer intensity in various narrow ranges of H-ion concentration. These values have therefore been



calculated from the titration data for each successive region of change of H-ion concentration, in pH units, with each successive addition of one cc. of 0.20 N acid or alkali to 100 cc. of the extract or suspension, as heretofore specified.

The following formula was used in this calculation:

$$\frac{\text{cc. acid or alkali added to produce pH change}}{\text{Av. Vol. of solution}} \times \left\{ \frac{\text{Normality factor of acid or alkali}}{\text{Change in pH units}} \right\}$$

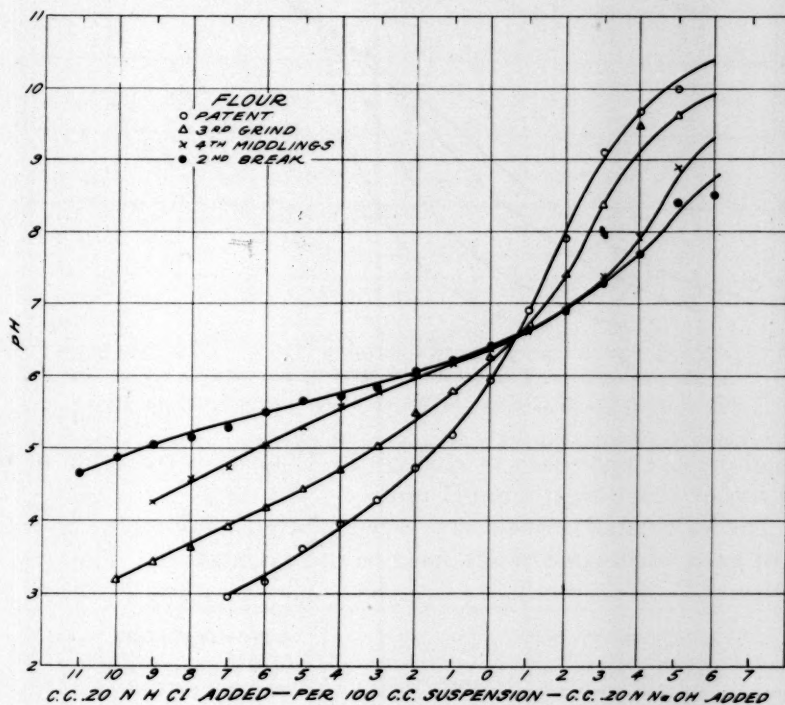


Fig. 3. Titration Data upon Soft Wheat Flour Suspensions

If (2.00 cc. and 4.00 cc.) of acid or alkali was each added to 100 cc. of extract and the difference in the resulting H-ion concentrations in pH units was 0.50, the substituted values would be as follows:

$$\frac{(4 - 2) \times 0.20}{\left(100 + \frac{4 + 2}{2}\right)} \times 0.50$$

In other words, the value obtained represents the equivalents

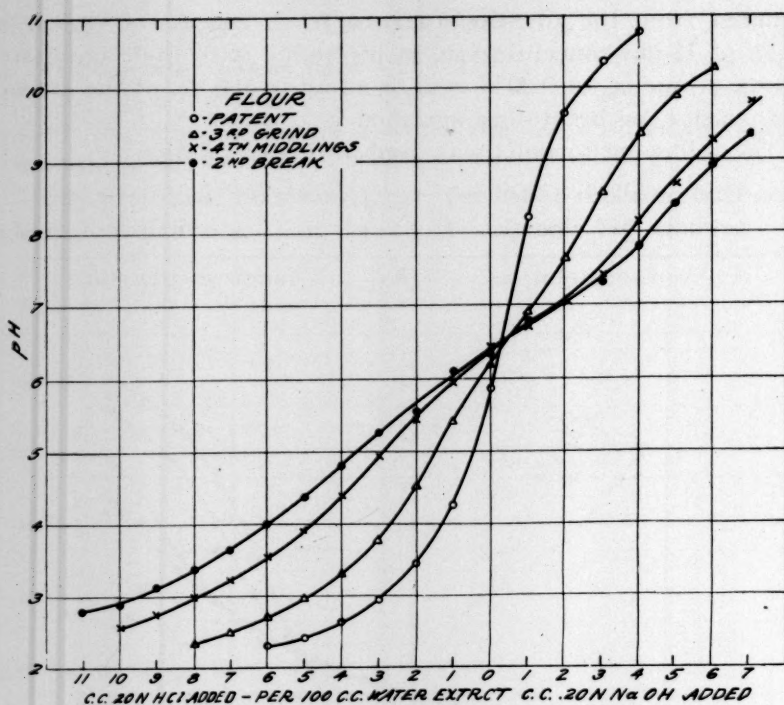
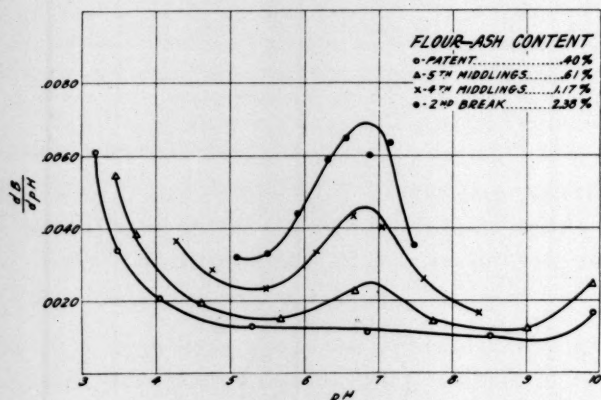


Fig. 4. Titration Data upon the Water Extracts of Soft Wheat Flours

of acid or base necessary to change the H-ion concentration of the solution or suspension one pH unit.

The calculated values have been plotted against the average pH of each successive range used in the calculations. The graphs

Fig. 5. Buffer Intensities of Water Extracts of Hard Spring Wheat Flours  
(Calculated from data of Bailey and Peterson)

in Figures 5, 6, 7, 8, and 9 indicate, therefore, the buffer intensity at different ranges of H-ion concentration.

The buffer capacity of each sample of flour is indicated roughly by the area prescribed by the middle portions of each curve. The increases in buffer intensity in the high acid and high alkaline ranges are due largely to normal acid and alkali buffering.

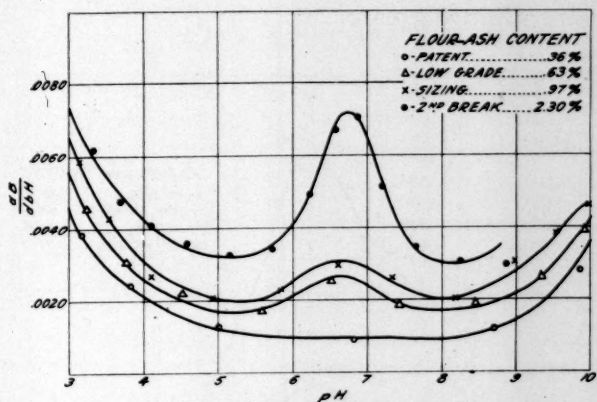


Fig. 6. Buffer Intensities of Water Extracts of Hard Winter Wheat Flours  
 (Calculated from data in Fig. 2.)

Comparisons of the relative buffer capacity and correlations of these values should therefore be confined to the same range of H-ion concentration, which should not extend too far into either the acid or the alkaline range.

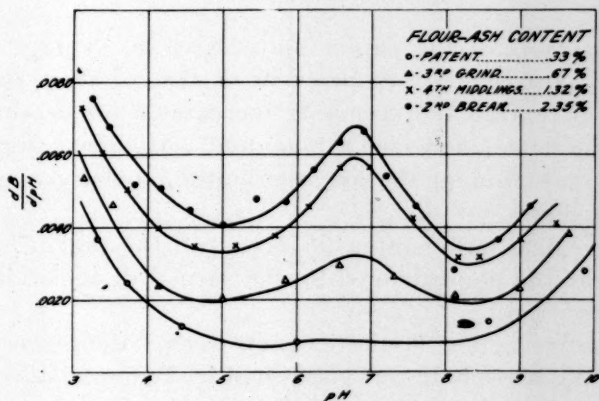


Fig. 7. Buffer Intensities of Water Extracts of Soft Wheat Flours  
 (Calculated from data in Fig. 4.)

The approximate average buffer intensity of each flour suspension and extract has been calculated between the limits of pH 4.50 and 8.50 and are given in Table III. The average buffer intensity for each percentage of ash content of each sample is also shown.

The figures indicate that the relative amounts of extractable buffers in hard spring and hard winter wheat flours of the same ash content are approximately the same; in soft winter wheat flours they are slightly greater.

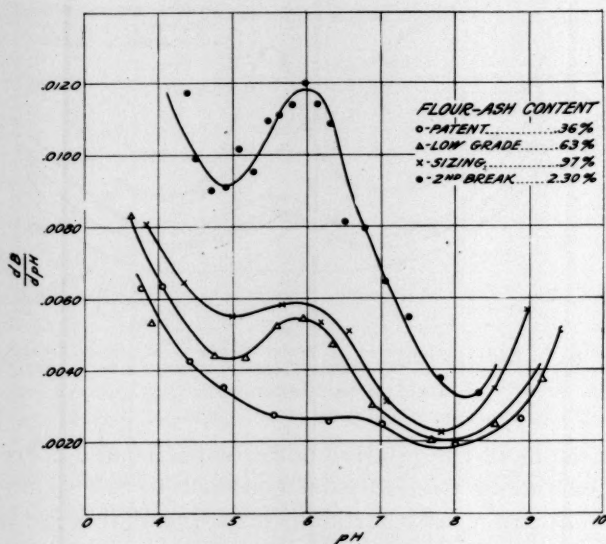


Fig. 8. Buffer Intensities of Hard Winter Wheat Flour Suspensions  
(Calculated from data in Fig. 1.)

The extracts of the patent flours have an average buffer intensity of approximately 38 per cent of that of their suspensions. The ratio of extractable amounts increases with decrease in the grade of the flour (increased ash content). However, for each percentage of ash content the average buffer intensity is greatest in the patent flours.

The greatest buffer intensity occurs in the region of pH 6.50-7.00, or near the point defined by the second dissociation constant of phosphoric acid.

The buffer action in the extracts seems therefore to be due mainly to the phosphates, as suggested by Bailey (1925).

To correlate the buffer capacity and the phosphorous content of the extracts and suspensions, the phosphorous content of the



TABLE III  
AVERAGE BUFFER INTENSITY OF WATER EXTRACTS AND SUSPENSIONS  
OF VARIOUS GRADES OF FLOUR OF DIFFERENT TYPES

Flours	Ash %	Average buffer intensity			
		Extract	Average buffer intensity Av. dB dpH/% Ash	Suspension	Average buffer intensity Av. dB dpH/% Ash
Hard spring wheat					
Patent	0.40	0.001125	0.00281		
5th middlings	0.61	.001572	.00258		
4th middlings	1.17	.00240	.00205		
2nd break	2.38	.00400(approx.)	.00168		
Hard winter wheat					
Patent	0.36	.00107	.00297	0.00282	0.00783
Low grade	0.63	.00196	.00265	.003616	.00574
Sizing	0.97	.00239	.00227	.00431	.00444
2nd break	2.30	.00408	.00178	.00753	.00328
Soft winter wheat					
Patent	0.33	.000942	.00285	.00244	.00740
3rd grind	0.67	.00244	.00364	.00384	.00573
4th middlings	1.32	.00394	.00298	.00597	.00454
2nd break	2.35	0.00472	0.00201	0.00771	0.00328

water extracts and the supernatant liquids of flour suspensions acidified with 12 cc. of 0.20 N HCl and allowed to stand for three hours were determined. The total phosphorous content as well as the phosphorous content of the extracts of two flours used are given in Table IV.

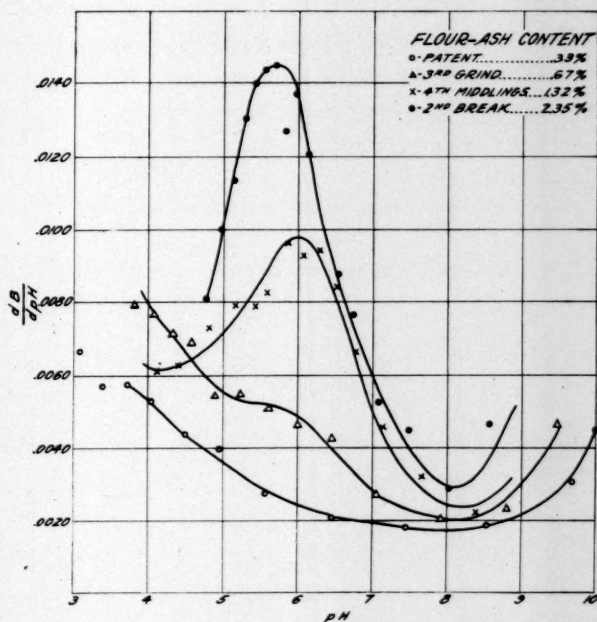


Fig. 9. Buffer Intensities of Soft Wheat Flour  
(Calculated from data in Fig. 3.)

The phosphorous content extracted by water is approximately 50 per cent of that of the flours. The increase of buffer capacity in the acid extracts, however, is greater than can be accounted for by the increase in phosphorous content on the basis of the values for the water extracts.

TABLE IV  
DISTRIBUTION OF PHOSPHORUS IN WATER AND ACID EXTRACTS OF TWO FLOURS

Flour	Ash	P <sub>2</sub> O <sub>5</sub>	P <sub>2</sub> O <sub>5</sub> in H <sub>2</sub> O extract on basis of flour	Per cent of total	P <sub>2</sub> O <sub>5</sub> in acid extract on basis of flour	Per cent of total
	%	%	%		%	
Hard winter wheat Low grade	0.63	0.317	0.167	52.7	0.1912	60.3
Soft winter wheat 4th middlings	1.32	0.757	0.420	55.5	0.581	76.8

### Summary

The buffer intensity of extracts and suspensions of different types and grades of flour, in different ranges of H-ion concentration, has been shown.

The water extract of all types of flour used shows a maximum buffer intensity in the same range of pH 6.50-7.00. In the suspensions, the zone of maximum buffer intensity occurs in the range of pH 5.75-6.25.

The average buffer intensity of the water extracts over a wide range of H-ion concentration, varies from approximately 38 per cent of the average of the suspension in the high grade flours, to approximately 62 per cent in the lower grades.

Buffer capacity is not strictly proportional to ash content. The correlation between buffer capacity and ash content is not the same for high grade as for low grade flours.

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# EFFECT OF VARIATION IN INGREDIENTS ON COLOR OF CHOCOLATE CAKE

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Color is an important factor in the consumer's preference for foods. Unbalanced diets may frequently be laid to foods unattractive in color. Pavlov (1927) and other scientists have proved that the psychological appeal has a definitely stimulating effect upon digestive processes.

Many means are used to make foods attractive in color. The preservation of the natural color of vegetables and fruits during cooking is given much consideration. The demand on the part of the consumer for highly colored foods and drinks has led to the use of artificial colors. The color of many foods as they come on the market is of economic value.

The baker, too, has his problems in producing desirable color effects. In no other baked product is there a greater variety of shades of color than in chocolate cake. They range from grayish yellow to rich mahogany. What one person may regard as most desirable is not necessarily that which will be preferred by all others. It is desirable, however, that a baker be able to produce the shade which is most desired by the majority of his customers and that he be able to produce this shade consistently.

Because of the effect of the ingredients of chocolate cake on its color, baking tests were made with variations in ingredients. Hydrogen-ion concentration, color, and flavor determinations were made.

## Experimental

Among the ingredients that may be expected to affect the color of the baked product are milk, soda, baking powder, salt, egg yolk, and the kind and quantity of chocolate. These were used as variants in studying the factors that affect color.

Eight series of baking tests were conducted, in which the following ingredients were used as the basic formula:

	Grams		Grams
Flour .....	128	Sucrose .....	200
Butter .....	53	Sodium chloride .....	1
Chocolate .....	57	Sodium bicarbonate .....	3
Egg .....	96	Water .....	158
Concentrated sour skimmilk.....		32 grams	

The method of incorporating the ingredients was as follows: A portion of the water was added to the soda, and the rest of the water was added to the concentrated sour skimmilk. The sugar, butter, and salt were creamed for 3 minutes in a Hobart mixer at medium speed. The eggs were gradually added during the next 3 minutes of beating. After the addition of the egg the beating was continued for 6 minutes. Care as to time and temperature was used in melting the chocolate, which was added to the creamed butter, sugar, salt, and egg, and the mixture was beaten at low speed for 60 seconds. The milk and soda solutions and the flour were alternately added to the creamed mass, with just enough stirring to incorporate the ingredients. After all ingredients were added, the mixture was stirred for 60 seconds at low speed. Throughout the mixing the ingredients were maintained at a temperature of 72°F.

The cake batters, each consisting of 453 grams, were baked in a pan of the following dimensions: top,  $5\frac{3}{4} \times 7\frac{1}{2}$  inches; bottom,  $4\frac{1}{2} \times 6\frac{1}{2}$  inches; height, 3 inches. They were baked for 43 minutes at 360°F.

On the day following the making of the cakes, color determinations were made by the Munsell system,<sup>1</sup> which is described by Cleland (1921) and by Nickerson (1929). It is based upon the psychological fact that color has three attributes: hue, brilliance, and chroma. Troland (1922), of the colorimetry committee of the Optical Society of America, defines these three terms as follows: "Hue is that attribute of certain colors in respect of which they differ characteristically from a gray of the same brilliance and which permits them to be classified as reddish, yellowish, greenish, bluish, or purplish." "Brilliance (or value) is that attribute of any color in respect of which it may be classified as equivalent to some member of a series of grays ranging between black and white." "Saturation (or chroma) is that attribute of all colors possessing a hue which determines their degree of difference from a gray of the same brilliance."

Hydrogen-ion determinations were made on the second day, according to the procedure described by Whittier and Grewe (1929) as the ball quinhydrone method.

<sup>1</sup> This report is made possible by the co-operation of the Bureau of Agricultural Economics, U. S. Dept. Agr., where the method of applying the Munsell System, including formulas and apparatus, has been developed by Miss Dorothy Nickerson, color technologist, in connection with the research program of the Division of Cotton Marketing and the standardization work of the Hay, Feed, and Seed Division.



**Series I. Effect of acidity of milk.**—Sweet, mildly acid, strongly acid, and concentrated sour skimmilk were used in the first series of cakes. The concentrated sour skimmilk was made by a procedure recently perfected in the Bureau of Dairy Industry. It has several very desirable features, chief of which are its good flavor in baked products; its high milk-solids content (27%); its acid content which can be definitely controlled and is of such a concentration as to be self-preserving. The process is described by Rogers, Johnson, and Alberty (1926). The results obtained on cakes made from these four milks are recorded in Table I. The acid content of the milk was found to be a very important factor in the color of chocolate cake. The cake made from the sweet milk was darkest, having a hue of 9.65 and a brilliance of 1.69. That made from the strongly acid milk was lightest, having a hue of 12.83 and a brilliance of 2.12. The attribute "chroma" was not significant in judging color of chocolate cake.

In order to have milk of definite acidity, concentrated sour skimmilk was used in the other series of this investigation.

TABLE I  
EFFECT OF ACIDITY OF MILK AND OF QUANTITY OF MILK SOLIDS ON COLOR OF CHOCOLATE CAKE

No.	Skim Milk	Munsell notation			H-ion concentration pH
		Hue Scale of 100	Brilliance Scale of 10	Chroma Scale of 10	
1	Sweet	9.65	1.69	1.50	7.09
2	Mildly acid	10.61	2.01	1.74	6.92
3	Strongly acid	12.83	2.12	1.42	6.23
4	Concentrated sour, 32 gm.	11.69	2.05	1.30	6.86
5	Concentrated sour, 64 gm.	11.80	2.05	1.18	6.75

**Series II. Effect of quantity of milk solids.**—The same amount of concentrated sour skimmilk as was used in the preceding series was used in one cake and 64 grams, or double the quantity, in another. As hydrogen-ion concentration was found to be a factor in the color of chocolate cake in the preceding series, excess sodium bicarbonate was used to neutralize the acidity of the extra milk. The data are recorded in Table I. The two cakes were much the same in color.

**Series III. Effect of the use of different brands of chocolate and cocoa.**—Variety of the cocoa bean and processes of manufacture are important factors in the color of chocolate and cocoa. It is to be expected that various brands of chocolate and cocoa will produce cakes of different color, consequently only two brands of each were used. The results obtained are recorded in Table II.

There was considerable difference in the color of the four cakes. Chocolate No. 2 was used in all the cakes except those in this series.

**Series IV. Effect of quantity of chocolate.**—Two cakes were made, one containing 57 grams (the basic formula) and the other 85 grams, one and one-half times the quantity of the former. The variation in absorption brought on by an increase in chocolate was not adjusted. The results obtained are recorded in Table II. Increase in quantity of chocolate resulted in a more highly colored cake. The cake containing 85 grams of chocolate had a hue of 10.40 and a brilliance of 1.65; that containing 57 grams of chocolate had a hue of 11.69 and a brilliance of 2.05.

TABLE II  
EFFECT OF BRAND AND QUANTITY OF CHOCOLATE AND COCOA ON COLOR OF CHOCOLATE CAKE

No.	Chocolate or cocoa	Munsell notation			H-ion concentration pH
		Hue Scale of 100	Brilliance Scale of 10	Chroma Scale of 10	
1	Chocolate No. 2	10.32	2.05	1.39	6.85
2	Cocoa No. 1	11.26	1.55	0.83	6.57
3	Cocoa No. 2	10.27	1.64	1.21	6.54
4	Chocolate No. 1, 57 gm.	11.69	2.05	1.30	6.86
5	Chocolate No. 1, 85 gm.	10.40	1.65	1.24	6.86

**Series V. Effect of quantity of sodium bicarbonate and of H-ion concentration.**—Cakes containing 1, 2, 3, 4, and 5 grams of sodium bicarbonate were made. The results obtained on color and H-ion concentration are recorded in Figures 1 and 2. The relationship of the H-ion concentration to hue is that of a curve, and to brilliance that of a straight line. This change in color when varying amounts of sodium bicarbonate are used and its effect on H-ion concentration confirm the findings in the first series, where milks with varying degrees of acidity were used and the conclusion was drawn that H-ion concentration of milk is a very important factor in the color of chocolate cake.

The color constituent of chocolate has the properties of an indicator over the range in which chocolate cake has desirable eating properties. It is yellow at a pH of 5.0 and increases in hue to red at a pH of about 7.5.

This change in color due to change in H-ion concentration has been observed with other baked products. Grewe (1926) found that the use of cream of tartar, through its effects upon H-ion concentration, was a factor in the color of angel cake. Stephens, Child, and Bailey (1928) observed that the excess of sodium bicarbonate

was a very important factor in the color of molasses cookies. The H-ion concentration of bread is a factor in its color. Tyrosine, sugar, and iron molecules are probably among those that change color as a result of change in H-ion concentration.

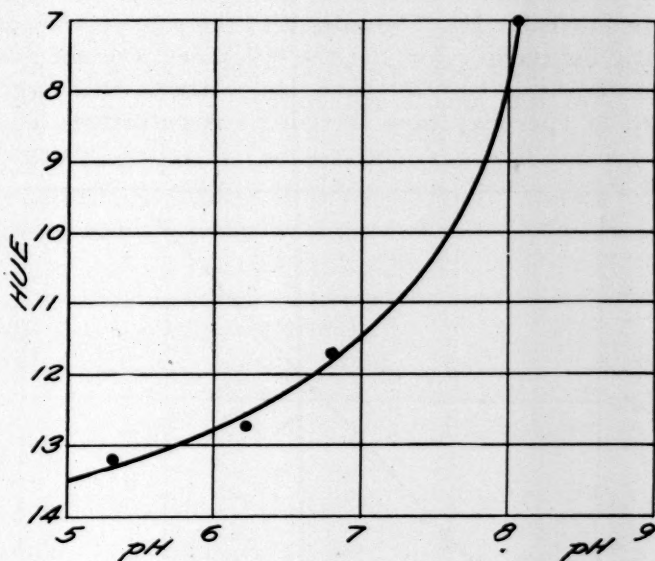


Fig. 1. Effect of Variation in H-Ion Concentration on Color, in Terms of Hue, of Chocolate Cake

**Series VI. Effect of salt.**—The effect of salt was studied by making two cakes, one according to the basic procedure and one with no salt. The results are recorded in Table III. It seems that, in the quantities usually found in chocolate cake, salt has little effect on color.

TABLE III  
EFFECT OF SALT, BAKING POWDER, AND COLOR OF EGG YOLK ON COLOR OF CHOCOLATE CAKE

No.	Variant	Munsell notation			H-ion concentration pH
		Hue Scale of 100	Brilliance Scale of 10	Chroma Scale of 10	
1	Standard	11.69	2.05	1.30	6.86
2	Salt, omitted	12.05	2.02	1.36	6.83
3	Baking powder, 3 gm.	12.06	1.98	0.96	6.89
4	Egg yolk, pale yellow	11.68	1.74	1.19	6.92
5	Egg yolk, reddish yellow	11.31	2.04	0.98	6.74

**Series VII. Effect of baking powder.**—In studying the effect of baking powder, one cake was made according to the basic procedure and in another 3.0 grams of baking powder was incorpor-

ated. The results are recorded in Table III. There was slight variation in the color of the two.

**Series VIII. Effect of color of egg.**—In studying the effect of the color of egg yolk two cakes were made, in one pale yellow egg yolks were used, in the other reddish yellow ones. The results are recorded in Table III. The cake with the pale yellow egg yolks was slightly lighter in color, but the difference was not great.

Sharp and Powell (1927) have demonstrated that egg whites, as a result of age, may vary in H-ion concentration. The above

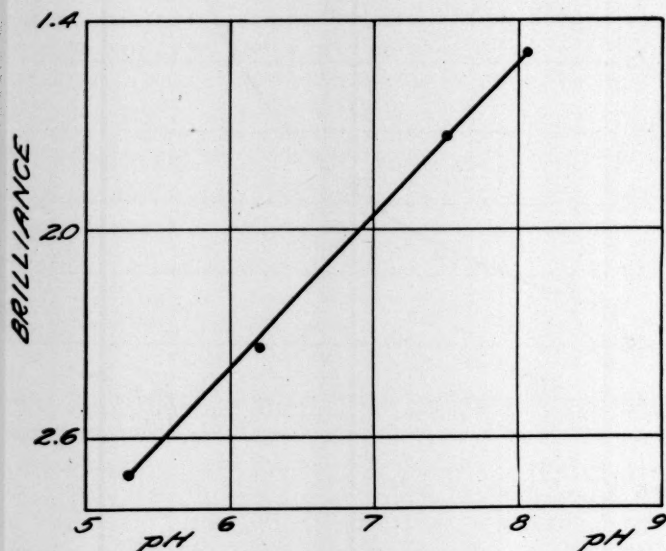


Fig. 2. Effect of Variation in H-Ion Concentration on Color, in Terms of Brilliance, of Chocolate Cake

data on the effect of acidity of milk and quantity of sodium bicarbonate indicate that H-ion concentration is a factor in the color of chocolate cake. It is to be anticipated that there will be a slight variation in color with variation in H-ion concentration of egg white.

**Flavor.**—The chief means of testing flavor is personal preference. What is most pleasing to one is not always most pleasing to another. Because of an insufficient number of judges, not much consideration was given to flavor except in the series in which sodium bicarbonate was the variant. It seems that sodium bicarbonate in quantities that do not raise the H-ion concentration above pH 8.0, does not produce detrimental effects. In the baking industry



there has been a preference for the use of sour milk in making chocolate cake. It is probable that its acid content gives desirable effects with chocolate flavor. By the use of sour milk and sufficient soda to produce a rich mahogany color, desirable flavor and color may be obtained.

### Summary

1. Eight series of investigations were made on the effect of variation in ingredients on the color of chocolate cake. Color determinations were made by means of the Munsell system.

2. Acidity of milk is a very important factor in color. Sweet milk produces a dark cake; strongly acid milk, a much lighter one. Variation in color is probably due to change in H-ion concentration.

3. Quantity of soda is an important factor—the effect is that of change in H-ion concentration.

4. Change in H-ion concentration results in change of color in terms of hue and brilliance. The relationship of H-ion concentration to hue is in the form of a curve and to brilliance in that of a straight line.

5. The color constituent of chocolate has the properties of an indicator. It is yellow at pH 5.0 and changes to red at pH 7.5.

6. Sodium bicarbonate may be used to produce a rich mahogany color, or in quantities resulting in a pH of 8.0, without producing detrimental effects on flavor.

7. Different brands of chocolate and cocoa produce cakes of different shades.

8. Quantity of chocolate is a factor in color. Increase in quantity of chocolate produces a darker and more highly colored cake.

9. Variation in quantity of salt and baking powder when used in the amounts found in baking practice, in quantity of milk solids, and in color of egg yolk are of minor importance.

The author wishes to acknowledge the assistance given by E. O. Whittier in making the H-ion determinations reported in this paper.

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## EVALUATING THE QUALITY OF WHEAT VARIETIES BY CO-OPERATIVE TESTS <sup>1</sup>

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(Read at the Convention, May, 1919)

One of the major lines of work of the Kansas Agricultural Experiment Station is to develop new wheat varieties that out-yield those grown at the present and that at the same time have superior milling and baking qualities. To determine these qualities is the task of the Department of Milling Industry.

It may not be necessary for the chemist in a flour mill to determine which of several flours made from sound and apparently good milling wheat is the best. But in wheat improvement work this very thing must be done. When the agronomist has determined that a variety is satisfactory from the grower's standpoint, it is then necessary to know if it will be satisfactory to the miller and the baker, and this must be determined before the wheat is increased for distribution and growing on a large scale. Sometimes this has not been done as carefully as it should have been done, and the result has been complaints from the millers and bakers. As a variety satisfactory to wheat growers will be grown on millions of acres a few years after distribution, it is important that none but the best varieties shall be distributed. After a new variety has shown itself promising in the wheat breeding nursery, it is grown

<sup>1</sup>Contribution No. 38 Department of Milling Industry.

for several years on 1/20 acre plots on the agronomy farm in order to establish its agronomic qualities. A careful study is made of milling and baking characteristics and chemical composition. A variety that continues to show superiority over old and tested wheats is next grown by co-operators for several years in various sections of the state. This serves to establish the adaptability of the variety to be grown on different soils and under different climatic conditions. Milling, baking, and chemical tests are continued. Only when a new wheat has been shown to have superior quality is it distributed.

Tenmarq is a new hybrid wheat that has been found to have several agronomic qualities superior to those of Turkey and, according to tests made in the Milling department, it also has milling and baking qualities equal if not superior to Turkey. However, in case of such importance as the milling and baking qualities of a new wheat, sole dependence should not be placed on the tests of one laboratory, especially as some of our methods are radically different from those used by some cereal chemists. It was therefore thought advisable to have tests made by several of these men. Most chemists were equipped to mill the wheat and to bake the flour. These received the wheat. Some did not have an experimental mill, and to them was sent the flour milled at Manhattan on an Allis experimental mill. The milling was done by a practical miller who mills about 500 samples of wheat a year.

The reports from these chemists have been assembled and studied. The chemists are indicated by letters, except for the Agricultural College, and each chemist has been informed which is his letter.

For these tests, 22 samples were available. The wheats were grown in 1928 at the experiment station at Manhattan and at the substations at Hays and Colby. Samples were obtained also, from co-operators in Harper, Edwards, Sedgwick, and Sumner Counties. The wheats from Harper and Edwards Counties were, as a class, low in protein. Only two chemists felt that they had time to test all of the 22 samples, but every chemist tested one or more of each of the four most important varieties under consideration, namely: Turkey, Blackhull, Superhard, and Tenmarq. The samples were submitted by number and none of the chemists knew the names of the varieties represented. Not until they had submitted their reports were the names of the varieties revealed. The ranking was made by number, and the writer has in this paper substituted the variety name.

### Chemist A

Chemist A used the proposed and tentatively adopted A. A. C. C. standard baking method with the modification he has found necessary with flours milled on a small Allis experimental mill. This consisted of the use of 5 per cent instead of 2.5 per cent sugar. This extra sugar necessitated a reduction of 1 per cent in absorption, making the absorption standard 57 instead of 58 on a 15 per cent moisture basis. He used the basic procedure with supplement C, involving the addition of 1 and 2 mg. potassium bromate, respectively, for each loaf. This chemist rated the varieties as follows in order of preference: (1) Superhard, (2) Kanred, (3) Blackhull and Early Blackhull, (4) Tenmarq and Turkey.

### Chemist B

Chemist B used the conventional baking method. In evaluating these wheats he stated that it was his belief that the results from those from Harper and Edwards Counties should be omitted from the comparisons. While some of the volumes were satisfactory, the crust and shred would condemn all of them for bakeshop practice. This was probably due to the low protein. The other samples he ranked in order of preference within each county as follows:

County where grown	Wheat variety
Sedgwick .....	Tenmarq Kanred Early Blackhull
Sumner .....	Tenmarq Kanred Superhard
Riley .....	Tenmarq Kanred Superhard Blackhull Early Blackhull

The conclusion from the work of Chemist B is almost diametrically opposed to that of Chemist A, who placed Tenmarq last and Superhard first. He states, however, that under certain soil and climatic conditions Turkey or Kanred would be more satisfactory than Tenmarq.

### Chemist C

Chemist C made blends of each of the four varieties. The tentative standard method of baking was used, with modification as indicated. He made two baking tests, one with  $2\frac{1}{2}$  per cent and



one with  $4\frac{1}{2}$  per cent sugar. The best results were obtained with the larger amounts. In evaluating the flours he says: "We have come to the conclusion that it is folly to attempt to say which of several sound flours is the best. One must know the conditions under which a flour must perform before he can safely judge its merits. For the class of trade this mill serves we can safely say that the flour milled from Superhard would be the least satisfactory." He finds it a problem to evaluate the other three, but is inclined to place them in the following order of preference: (1) Blackhull, (2) Tenmarq, (3) Turkey.

Chemist C disagrees with Chemist B in regard to Blackhull. However, this is not of much consequence as he is inclined to find only minor differences among Tenmarq, Blackhull, and Turkey, but is in no doubt about placing Superhard last. His reason for placing Tenmarq below Blackhull is the low resistance of the former to bromate. The inference is that this means low resistance to mechanical action. This disagrees entirely with our findings, as we have found Tenmarq flour the most highly resistant to mechanical action.

#### Chemist D

Chemist D used essentially the proposed method of the A. A. C. C. In addition, he studied stimulation as effected by the use of  $\frac{1}{2}$  to one per cent Arkady. By this means, information was sought in regard to the way gluten acts towards oxidizing agents.

Chemist D rated the wheats in order of preference as follows:

- | High Protein Wheats           | Low Protein Wheats          |
|-------------------------------|-----------------------------|
| 1. Tenmarq, Manhattan         | 1. Turkey, Harper County    |
| 2. Blackhull, Manhattan       | 2. Blackhull, Harper County |
| 3. Kanred, Manhattan          | 3. Tenmarq, Harper County   |
| 4. Superhard, Manhattan       | 4. Superhard, Harper County |
| 5. Early Blackhull, Manhattan |                             |

Tenmarq was placed first among the high protein wheats, and third among the low protein wheats. In each group Superhard was placed fourth. The rating of these wheats was on the basis of making a baker's flour. According to this chemist, the low protein wheats are less valuable for making baker's flour than the high protein wheats regardless of variety. In making a family flour, the low protein wheats would class equally well with the high protein wheats; that is, they would make an excellent family blend.

#### Chemist E

Chemist E used the conventional baking method. Unfortunately, his ratings were not obtained, but an attempt was made to

do this on the basis of the figures he submitted, paying most attention to texture and loaf volume. Each locality is considered separately.

Where Grown	Wheat Variety	Where Grown	Wheat Variety
Manhattan	1. Blackhull	Edwards County	1. Tenmarq
	2. Tenmarq		2. Blackhull
	3. Kanred		3. Turkey
	4. Superhard		4. Superhard
	5. Early Blackhull	Sedgwick County	1. Tenmarq
Harper County	1. Blackhull		2. Early Blackhull
	2. Tenmarq		3. Kanred
	3. Turkey	Sumner County	1. Tenmarq
	4. Superhard		2. Kanred
			3. Superhard

Tenmarq has three firsts and two seconds, Blackhull has two firsts and one second. Kanred and Turkey have second or third place. These wheats as varieties have given satisfaction to the trade. Superhard has fourth or last place. A fair conclusion from this report would be that there are only minor differences among Blackhull, Turkey, and Tenmarq, but that Superhard is least desirable.

This chemist also made blends from the flours of the four most important wheats, and the loaves from the blends were rated as follows: Tenmarq, Blackhull, Kanred, Superhard.

### Chemist F

Seven 100-pound samples of wheat, one each of Kanred, Turkey, and Superhard; and two each of Tenmarq and Blackhull, were sent to Chemist F, as he had facilities for milling and baking larger samples. The following information was given by the head miller, in charge of the milling tests. "From 4 to 6 pounds of water were added to each of the seven wheat samples and they were all tempered for approximately 14 hours. According to our weights and figuring a straight grade of flour, these samples, based on clean wheat to the rolls, would yield around 4:30. Bran from all samples was a nice thin flake, but looked pale. Tenmarq ground very nice and the bran was of light nature. The middlings were firm and were readily reduced to flour. Blackhull was very similar in its behavior. Tenmarq was quite a bit different from the rest. It milled nice, but I had to grind very high or else the bran coat which seemed very thin would grind right into powder."

According to the milling report these wheats were the same in yield. Tenmarq was a good milling wheat, and the blend was similar to that from Blackhull. No objection was made to Superhard from the milling standpoint.

In baking "the doughs were made according to our standard straight dough formula and given the same fermentation time, namely, three hours with two punches intervening. The volume figures represent the average of four 1½ pound loaves selected at random from each batch." Tenmarq, which our head miller mentioned as being "quite different from the rest," produced bread of the largest volume and the highest score. The scoring was made on the basis of the American Institute of Baking.

This chemist did not definitely rate all the samples, but from his results it appears that Tenmarq grown at Manhattan was the best, and the blend of Superhard the poorest. The pure Tenmarq from the Agronomy Farm had the highest protein content, and the blend of Tenmarq from other places the lowest of all the samples. In spite of this low protein, it had a higher bread score than the blends of Blackhull, Turkey, and Superhard.

A fair conclusion from his report would be that Tenmarq is as good a wheat as, if not better than, any of the other varieties tested.

### Chemist G

Chemist G made very extensive chemical determinations, and the milling and baking tests were repeated six weeks apart. Baking tests were made on both the natural and the bleached flours. On the basis of his work he listed the wheats by number in the order of quality: (1) Tenmarq, Manhattan; (2) Tenmarq, Harper County; (3) Blackhull, Manhattan; (4) Blackhull, Harper County; (5) Kanred, Manhattan; (6) Turkey, Harper County; (7) Superhard, Manhattan; (8) Superhard, Harper County.

With his method of testing he secured as good results from Blackhull as from Turkey or Kanred. Tenmarq was rated superior to Turkey and Kanred. He placed Superhard as the poorest in quality and accurately identified the two samples.

### Chemist H

Chemist H milled and baked all the samples from the 22 wheats. The most significant data obtained were averaged and the results are given in Table I. As Kanred is a strain of Turkey wheat, it was averaged with the latter. On the three counts loaf

volume, color, and texture, Tenmarq so far excels the others as to leave no doubt that it is a superior wheat. On the score of loaf volume and texture, Superhard is significantly inferior to Kanred, Turkey, and Blackhull. These differences found by Chemist H are great enough to brand Superhard at least as having a quality that should be seriously questioned before recommending this wheat to growers. On only one point was Superhard found to be slightly superior to the others, viz., absorption.

TABLE I  
COMPARISONS OF FOUR VARIETIES OF WHEAT BY CHEMIST H

Variety	Weight per bushel	Flour yield	Protein, in wheat	Ash in flour	Absorp- tion	Loaf volume	Texture, score	Color, score
	lb.	%	%	%	%	cc.		
Tenmarq	59.1	77.5	11.6	0.47	60.1	2150	85.0	85.5
Turkey and Kanred	59.1	77.1	11.9	.49	60.7	2180	76.5	78.0
Blackhull	60.0	73.0	11.0	.48	58.3	2100	76.5	81.0
Superhard	60.3	77.3	11.6	0.50	61.1	1990	69.0	78.5

Four chemists did not have facilities for making milling tests, and they were supplied with flour. Chemist I obtained flour from the samples milled by Chemist E. Flour milled on the experimental mill at Manhattan was furnished to the rest.

### Chemist I

Chemist I used blends made by taking equal parts of flour from the wheats grown in Harper and Edwards Counties, and from variety test plots at Manhattan, Hayes, and Colby. Fermentation tolerance, buffer action, resistance to mechanical action, and leeway periods were also determined. On the basis of all tests he rated Tenmarq first, Turkey second, Blackhull third, and Superhard last.

### Chemist J

Chemist J states in regard to methods: "We are using an average commercial formula and find it gives us more reliable results than any other method we have tried heretofore. We have found the fermentation period of very great importance, but in our test work do not vary it to suit the flour." In ranking these flours on the basis of quality he says: "While not attempting to comment on each sample, Tenmarq grown at Manhattan stands at the top and it is interesting to note that it is highest in protein." "While probably there is a tendency for quality to follow the protein, it is not true in all cases, which is particularly outstanding in Blackhull with an 8.90 protein and a volume of 95, fully equal



to Blackhull with 11.80 protein and 95 volume." According to this chemist nearly 3 per cent spread in protein made no difference in the baking results, which shows that quality of protein is of at least as great importance as quantity.

### Chemist K

Blends were made for this chemist of flours from each variety of wheat grown in different places. The baking formula used was as follows:

	Grams		Grams
Flour .....	700	Yeast .....	9
Sweet condensed milk.....	20	Lard .....	18
Salt .....	15	Sugar .....	21

The mixing was done in a Bachmann or a Fleischmann mixer at a temperature of 78°F. The punching time was gaged in per cent of total fermentation time as follows:

First punch, 75 per cent  
Second punch, 18¾ per cent

Third, or  
Panning, 6¾ per cent

The temperature of the fermentation cabinet was 80°F. All doughs were scaled previous to moulding to a constant weight of 510 grams. They were then placed in an automatic proof box and proofed to a constant dough volume of 75 cubic inches after which they were baked for 30 minutes. The loaf volume minus the constant dough volume gives the oven spring.

In evaluating these flours according to quality Chemist K ranks them as follows: Blackhull, by far the best of the group; Turkey, second; Superhard, third; Tenmarq, fourth.

In regard to the last two, Superhard and Tenmarq, he states "It is my opinion that these two flours are of poor baking value." In regard to Blackhull he says: "This should meet the requirements of some bakers altho it is not a strong flour. It exhibits a decided weakness when fermentation periods of 4 to 4½ hours are applied, as the volume rapidly decreases."

### Chemist L

Chemist L baked four samples of flour from each of the three places: Manhattan, Harper County, and Edwards County. The ranking was done on the 12 loaves and then on each set of 4 loaves. In one set Tenmarq had the first place, and in another, the lowest. Blackhull follows with second, third, and fourth places. In the group ranking, Blackhull has two firsts and one second; Tenmarq

has one first, one third, and one fourth. Superhard has sixth, eighth, and tenth place in the whole lot; two fourths and one second in the group ranking. According to this, Blackhull would be first, Superhard last, with Turkey, Kanred, and Tenmarq occupying intermediate positions.

Chemist L also made blends of these flours. On the basis of results secured from the blends he classed the flours as follows: Blackhull, Tenmarq, Kanred, Turkey, Superhard. The results on the blends give about the same evaluation as the baking of each flour by itself.

#### **Chemist M (K. S. A. C.)**

In our own laboratory we baked all samples by two methods. One may be called "severe" and the other "gentle." The latter is much like the conventional method used by most of the mill chemists. The dough is mixed for  $1\frac{1}{2}$  minutes in a special high-speed mixer. This mixing thoroly develops the dough and is probably equivalent to the amount of mixing done in 15 minutes in a large bake shop high-speed mixer. We judge this by the equivalent amount of dough development secured. The dough is then allowed to rise in an expansion cylinder for 100 minutes, after which it is moulded and placed in a tall round pan. This pan has a plunger by means of which it is easy to have all doughs rise to the same volume. The rise of the plunger in the oven measures the oven rise in cubic meters. The baking time is 40 minutes at  $240^{\circ}\text{C}$ . The longer time is needed because of the closed pan.

In the severe method, the dough is mixed for 5 minutes at high speed, which would probably be equivalent to about 50 minutes in a high-speed commercial mixer. No gluten can be washed from such dough. The dough is then moulded, placed at once in a pan, and allowed to rise the standard amount, after which it is baked. Dough treated in this way will not stand fermentation before panning. The method is difficult to carry out, because the dough is soft and sticky. It is absolutely necessary to have the right amount of water for mixing the dough. It is of advantage to use lactic acid in the formula, the same as is used for no-time dough.

The most significant figures in our tests are those for loaf volume and texture. By multiplying these figures a product is obtained that indicates the relative values of the loaves. This product for different samples is given in Table II, the last three digits being omitted.

With the gentle method, one variety averages nearly the same as another; with the severe method, there is a vast difference between Blackhull and Superhard, on the one hand, and Tenmarq and Turkey on the other.

TABLE II  
RELATIVE LOAF VOLUME AND TEXTURE OF WHEAT VARIETIES MILLED AND BAKED AT K. S. A. C.

Varieties	Severe method			Gentle method		
	Loaf volume	Texture score	Relative value	Loaf volume	Texture score	Relative value
Tenmarq	cc.			cc.		
Manhattan	2050	98	201	1810	97	176
Harper County	2135	98	209	1730	90	156
Edwards County	1985	93	185	1740	95	165
Sedgwick County	2150	99	213	1735	92	160
Sumner County	2130	97	207	1960	97	190
Sum	10450	485	1015	8975	471	847
Average	2090	97	203	1795	94	169
Kanred or Turkey						
Manhattan	1980	97	192	1690	90	152
Harper County	1860	94	175	1745	92	171
Edwards County	2140	98	210	1615	90	145
Sedgwick County	2070	99	204	1920	94	180
Sumner County	1930	94	181	2010	97	194
Sum	9980	482	962	8980	463	842
Average	1996	96	192	1796	93	168
Blackhull						
Manhattan	1580	83	131	1740	95	165
Harper County	1750	90	158	1785	92	164
Edwards County	1830	89	163	1745	95	166
Sedgwick County	1715	90	154	1790	92	164
Sum	6875	352	606	7060	374	659
Average	1719	88	152	1765	94	165
Superhard						
Manhattan	1650	85	140	1760	94	165
Harper County	1720	85	146	1750	90	158
Edwards County	1830	88	161	1805	97	175
Sumner County	1730	88	152	1930	94	181
Sum	6930	346	599	7245	375	679
Average	1733	87	150	1811	94	170

We have obtained similar results on hundreds of samples grown in all parts of Kansas. We have interpreted this as indicating that Blackhull and Superhard have low resistance to mechanical action.

This may mean simply that Tenmarq and Turkey have a greater resistance to mechanical action, which is of importance only in bake shops where severe mixing and dough handling methods are used.

If the results from the wheats above 11 per cent in protein and also below this per cent are averaged, the following figures are obtained:

TABLE III  
EFFECT OF PROTEIN CONTENT ON LOAF VOLUME AND TEXTURE

Protein	Severe Method			Gentle Method	
	Protein	Loaf volume	Texture score	Loaf volume	Texture score
	%	cc.		cc.	
Average above 11%	11.76	1920	94	1821	93
Below 11%	10.31	1855	92	1720	93

The higher protein wheats gave higher average texture and loaf volume. There were numerous exceptions to this, but as a rule the higher protein wheats give better insurance of success.

### Chemist N

Chemist N made a very extensive investigation on 16 samples. From his figures it was not apparent that one wheat is better than another from the variety standpoint. In his remarks the qualification "weak" or "only fair strength" was used to describe all wheats whose protein content was 11 per cent or below. Some of these were described as very weak, or not very good for bread flours. The wheats that had above 12 per cent protein were described as having good strength or very strong. In other words, very good for bread flours. It seems that the methods used by this chemist distinctly favor high protein wheats. This tendency in a less degree was noted with several other chemists. It seems that with their methods if a flour has high protein, it gives good results, and if low protein, poor results. This seems to be a defect in the baking test, as it does not lay sufficient emphasis on quality in protein.

### Chemist O

To Chemist O were sent four samples of wheat grown in the plant breeding nursery at Manhattan, Kansas—Blackhull, Tenmarq, Superhard, and Kanred. He found all to be alike in absorption. The baking formula included  $2\frac{1}{2}$  per cent yeast and  $1\frac{1}{2}$  per cent salt. The following statements and data are gleaned from the report on these four samples. "All four were very handsome in appearance; they were hard red and appeared closely related to the well known Turkey variety." "Superhard bit harder than the other and was the driest." "All milled excellently, tho some extra smooth roll work was necessary . . . in order to get a high extraction."



Chemist O determined the gas production of the flours and found it unsatisfactory in each case. "Such strong flours as these would be used . . . either for blending with weaker flours, in which case the gas deficiency would be overcome to a marked extent, or even entirely by including some exceptionally good gasers; or alone for sponging, in which case poor gasing is less important."

"All made up into good bodied tin doughs, and were very tough and elastic, the toughness being very striking. Tenmarq and Kanred were closely similar in these respects; Blackhull and Superhard being less tough." "At scaling, Tenmarq and Kanred were again the toughest and were closely similar; Blackhull was less tough and Superhard was less tough than Blackhull having slackened a little. During final proof, all except Blackhull worked well and showed good stability."

The following remarks are made about the loaves. "Tenmarq was of excellent volume and good outside appearance and crust, close and even grain, and good spring of crumb." "In all characters it was the best loaf of the series." "Superhard was of very good volume, outside appearance and crust being slightly inferior to Tenmarq. Kanred was similar in most characters to Superhard. Crumb color was slightly inferior, but better than Superhard."

"In order of merit the flours may be arranged as follows: Tenmarq best, Kanred, Superhard, and Blackhull easily the poorest."

#### **Chemist P**

Chemist P received flours from Tenmarq, Kanred, Blackhull, and Superhard wheats grown in the wheat nursery at Manhattan. He preferred Tenmarq, as far as appearance of the grain was concerned. He did not like to base an opinion as regards what he calls "strength" upon the absolute percentages of protein. In his opinion it is better to ascertain the percentages of gluten, not so much for the absolute figure, but to give the operator who has had long experience an opportunity to form an opinion as to the quality of gluten. "Although Tenmarq gave approximately  $\frac{1}{2}$  per cent less gluten than the other three, we prefer it." From the baking method used it was discovered that all four flours could be baked with the same process, but it was also discovered that it was desirable to use some yeast food to make sure of getting sufficient gas during the proofing period. "According to this test we again preferred Tenmarq." "We then baked all four by themselves and with

the small quantities of flour remaining made a second baking test using a blend of 50-50, one-half being flour obtained exclusively from our very ordinary wheat. On the basis of this test, particularly the way the doughs behaved, and the results obtained from both the 100 per cent and the 50 per cent trials, we again prefer Tenmarq, even tho the volume of its 100 per cent loaf was rather less than the others. This flour behaved better in the blend than the other. It seems to us that the 'runner up' is Kanred."

Thus on four counts, appearance of the wheat, quality of the gluten, gas producing ability, and bread score, Chemist P classes Tenmarq first. He placed Kanred second, and expressed no preference between Blackhull and Superhard.

### Summary

A summary of the ranking of these wheats by the seventeen co-operating chemists is given below.

TABLE IV  
RANKING OF WHEAT VARIETIES BY SEVENTEEN CEREAL CHEMISTS

Chemist	Rank			
	1	2	3	4
A	Superhard	Kanred	Blackhull	Tenmarq
B	Tenmarq	Kanred	Early Blackhull	Turkey
C	Blackhull	Tenmarq	Superhard	Blackhull
D (Manhattan)	Tenmarq	Blackhull	Turkey	Superhard
D (Harper County)	Turkey	Blackhull	Kanred	Superhard
E	Tenmarq	Tenmarq	Tenmarq	Superhard
F	Tenmarq	Blackhull	Kanred	Superhard
G (Manhattan)	Tenmarq	No preference	Superhard	Superhard
G (Harper County)	Tenmarq	Blackhull	Kanred	Superhard
H	Tenmarq	Turkey	Turkey	Superhard
I	Tenmarq	Turkey	Blackhull	Superhard
J	Tenmarq	No preference among the others.	Superhard	Tenmarq
K	Blackhull	Turkey	Kanred	Turkey
L	Blackhull	Tenmarq	Blackhull	Superhard
M	Tenmarq	Turkey	Blackhull	Superhard
N	Evaluation mostly on the basis of protein.			
O	Tenmarq	Kanred	Superhard	Blackhull
P	Tenmarq	Kanred	No choice.	

\* Total, 18.

Tenmarq: 12 first, 2 second, 1 third, 2 last.

Kanred and Turkey: 1 first, 10 second, 5 third, 2 last.

Blackhull: 3 first, 4 second, 5 third, 2 last.

Superhard: 1 first, 0 second, 3 third, 11 last.

The consensus of opinion seems easily in favor of Tenmarq, with Superhard in last place. Blackhull appears to contend for second and third places with Turkey and Kanred.

## VALUE OF THE VISCOSIMETER IN A COMMERCIAL FLOUR MILL LABORATORY

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It is not the purpose of this article to deal with the technical side of the viscosity test. Numerous scholarly papers cover practically every angle of this phase of the subject; however, the practical side dealing with the real value of this test to the commercial miller has been scarcely touched. Because of this, the writers have just completed a carefully planned investigation covering several months, during which time several thousand viscosity tests were made on every conceivable brand and grade of flour. Ideas and help were solicited from every source imaginable. We are especially indebted to Dr. C. O. Swanson and Dr. C. H. Bailey for many valuable suggestions.

A careful survey of what has been done with the viscosimeter in flour mill laboratories reveals the fact that there is no accepted standard method of operating this machine. We found no two investigators using exactly the same method. This limits the test almost entirely to the laboratory where the test is made. However, if there were an accepted standard method of carrying out the test, enough of the personal element of the operator enters to make it hard for the same reading to be obtained by a different operator in a different laboratory or even in the same laboratory.

All our tests were made with the new Mac Michael viscosimeter, which operates on the torsion principle. Great care was taken to have all solutions at room temperature—close to 70 degrees F.—and the viscosimeter warmed and running steadily before any tests were made.

The experiments were begun by using a mixture of 20 grams of flour and 100 cc. of distilled water. This mixture was stirred and shaken vigorously for about ten minutes, then poured into the viscosimeter bowl and a test made. Tests made in this way often did not check because of the difference in granulation which caused large differences in viscosity, therefore we found by experimenting that it was much better to let the flour and water mixture stand for one hour, during which time the mixture was thoroly shaken every ten minutes. The hour period had the added advantage of

allowing more time for making the test, because a variation of a few minutes makes less difference in the result than when a shorter period is used. This makes it possible to save time by carrying several tests simultaneously. To this flour and water suspension was added 0.5 cc. of a 50 per cent lactic acid solution, the mixture was thoroly shaken or stirred and poured into the bowl of the viscosimeter, and the machine was run until a reading could be obtained. One cc. of concentrated lactic acid was then added to the mixture in the bowl and thoroly stirred with the plunger, after which the machine was again started and a second reading made. This second reading was in most cases not so erratic as the first, but seemed to be more uniform than when the first reading was omitted. In many cases a third reading was taken after adding an oxidizer such as a drop of hydrogen peroxide or potassium bromate solution, but the third reading gave no more information than the second.

These experiments were begun by running the viscosimeter at the recommended speed of 20 r.p.m., but it was soon discovered that constant checking and much care were needed to keep the machine running steadily at that speed, therefore the governor was loosened to allow the machine to run freely at 32 r.p.m., at which speed it would run steadily from day to day with little checking.

The next difficulty was in reading the result of the test. We found that many, if not all, of the cereal chemists who use a viscosimeter were using a No. 30 B and S gauge wire. We found this wire satisfactory for low grade and low-protein flour but with high-protein flour the disk would swing around so far that it caused a rapid retardation and frequently a rather violent pendulum-like oscillation caused by a decrease in viscosity, which is attributed to syneresis. To counteract this, we changed to No. 26 B and S gauge wire.

This materially lowered our readings but enabled us to repeat the results with little variation. This lower reading was immaterial, as the readings were not intended for use outside our own laboratory. The sole purpose of the viscosity test, so far as we were concerned, was to find some test for the quality of protein and add another check on the mill in addition to the protein, ash, and moisture tests, with the hope that a more uniform flour would be the result. It was hoped that the viscosity test would indicate something of the kind of bread the flour would make without waiting for the baking test.



We read the result of the test when the disc retards from the initial swing to a point at which it stops for a short time before it starts to swing steadily back toward the zero point because of a decrease in viscosity as above explained. Some operators read the point reached on the first swing of the disc just before it starts to retard, but we found greater variation between readings made at this point than between readings made at the stopping point on the retard.

We found in every case that the higher the protein, the higher the viscosity reading when the comparison is kept within the same milling grade. This led us to believe that protein and ash content had much to do with the viscosity reading. We, therefore, scaled the amount of flour used according to the protein that it carried, using as a standard 20 grams of a flour carrying 10% protein. A flour carrying less than 10% protein was allowed proportionately more than 20 grams in the test and if of more than 10% protein, less than 20 grams was used. This seemed to eliminate the effect of the variation in protein content. It is possible to make this variation in the amount of flour used without interfering with the accuracy of the test, because the bulk of the endosperm of the wheat berry is composed of starch and numerous tests showed that a suspension of pure wheat starch in water gives a viscosity reading so low that it can be disregarded. Many tests showed the viscosity of pure wheat starch to be practically the same as that found on the same quantity of clear water.

In order to learn the part that the ash might play in these tests, we made a solution containing as nearly as possible the constituents of flour ash and added it in varying amounts to a sample of flour. In every case, the ash solution reduced the viscosity reading in proportion to the amount added. One-half per cent of this flour-ash solution added to a high-protein short patent flour will reduce the viscosity to that found in a low-grade flour or below. There may be some question as to whether or not the addition of this flour-ash solution has the same effect on viscosity as raising the ash content of flour in the usual way; nevertheless, we found that in every case where we could get two flours whose only difference was in ash content, the one having the higher percentage of ash always showed the lower viscosity. We were now convinced that the protein and ash content greatly affected the viscosity reading, but as we were interested only in what this test would tell us about quality, we supplemented all these tests with baking tests.

A sample of our best short patent high-protein flour was placed in an oven for three hours at a temperature of 120°C., after which a baking test showed the flour to be entirely dead and it will be referred to as "dead flour."

Viscosity tests checked with baking tests were made on various mixtures consisting of different percentages of the dead flour mixed with flour exactly like the dead flour had been before it was heated. The viscosimeter did not detect the dead flour, until at least 60 per cent of it was included in the mixture. The baking test easily detected as little as 10 per cent.

### Summary and Conclusions

The conclusions to be drawn from the experiments discussed appear to us unmistakable. No method of using the viscosimeter is well enough standardized or widely enough used to be called the correct method, therefore the results are of little value outside the laboratory where obtained.

In order to get at the quality of gluten, it was necessary to eliminate the effect of varying amounts of protein, which was done by having the percentage of protein in the solution constant instead of holding the weight of the flour constant.

The amount of ash in the flour was found greatly to affect the viscosity.

Our final conclusion was that the viscosity test adds nothing to the information now obtained from the protein and ash tests and can never be made to take the place of the baking tests.

## NEW AIDS IN THE ASHING OF FLOUR

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The ashing of flour is attended by difficulties, which would be eliminated by a reagent that would:

1. Fix inorganic acid radicals.
2. Reduce its excess to a definite compound, preferably a non-hygroscopic oxide.
3. Confer non-hygroscopicity on the incinerated residue.
4. Render infusible at ashing temperatures the incinerated residue.
5. Accelerate combustion.

Obviously the salts of the alkali and the alkali earth metals do not possess all these properties, therefore are of limited value as aids in the ashing of flour. It is also obvious that salts of the heavy and the noble metals cannot be used as such and need not be considered, as they form into uncertain and variable residues when heated with organic substances like flour. However, such objections cannot be postulated against certain of the earth metals occurring in the third and fourth groups of the periodic system, particularly the more basic elements like zirconium, lanthanum, yttrium, cerium, and thorium. These are available in the form of water-soluble salts (nitrates, acetates, etc.), which decompose into oxides by incineration, and these oxides, as is well known, are fairly non-hygroscopic and stable otherwise. Several other considerations, such as infusibility, non-volatility, and general chemical reactivity, suggest that these elements in the form of the water-soluble salts named may prove more useful in flour ashing than any reagents heretofore used. The possibility of using such salts of lanthanum, yttrium, cerium, and thorium as aids in flour ashing became still more apparent as a result of a few preliminary tests that especially demonstrated their accelerating action upon the combustion of the charred residues from flour.

This accelerating action was tested further by the following general procedure: Ten cubic centimeters of 40% alcohol, containing the desired weight of the metallic oxide in the form of a nitrate, were mixed into 5 gm. of flour contained in a flat-bottomed silica dish 65 mm. in diameter. The dish was then introduced di-

rectly into a muffle already heated to the desired temperature and the time was noted for the formation of a carbon-free ash, counting time from the moment the dish was introduced into the muffle.

This general procedure was followed in testing the accelerating effects of the oxides of lanthanum, yttrium, cerium, and thorium<sup>1</sup> in amounts ranging from 5 to 80 mg. on 5 gm. samples of a commercial soft wheat flour and of a Minneapolis hard wheat flour, both ashed at two different temperatures—cherry red and bright red. The data, to some degree approximated, are contained in Tables I and II and in Figures 1 and 2.

TABLE I  
TIME REQUIRED FOR ASHING 5 GRAMS OF SOFT WHEAT FLOUR WITH AMOUNTS OF OXIDES OF ELEMENTS INDICATED

Milligrams of oxide present	Temperature	La <sub>2</sub> O <sub>3</sub>	Y <sub>2</sub> O <sub>3</sub>	Ce <sub>2</sub> O <sub>3</sub>	ThO <sub>2</sub>
		min.	min.	min.	min.
80	Bright red	14	11	12	13
	Cherry red	17	16	14	15
40	Bright red	15	12	14	14
	Cherry red	17	17	15	16
20	Bright red	16	12	15	15
	Cherry red	17	17	17	17
10	Bright red	17	14	16	17
	Cherry red	19	17	17	19
5	Bright red	18	15	17	19
	Cherry red	23	20	20	22

It should be noted that with respect to muffle temperature, size and shape of dish, size of sample, etc., the above conditions for ashing are essentially the same as those ordinarily employed in cereal control laboratories. Accordingly, by the use of 5 to 20 mg. of the oxide of any of the above metals, it should be possible and

TABLE II  
TIME REQUIRED FOR ASHING 5 GRAMS OF HARD WHEAT FLOUR WITH AMOUNTS OF OXIDES OF ELEMENTS INDICATED

Milligrams of oxide present	Temperature	La <sub>2</sub> O <sub>3</sub>	Y <sub>2</sub> O <sub>3</sub>	Ce <sub>2</sub> O <sub>3</sub>	ThO <sub>2</sub>
		min.	min.	min.	min.
80	Bright red	12	12	13	14
	Cherry red	16	16	17	16
40	Bright red	13	13	13	14
	Cherry red	16	20	17	18
20	Bright red	14	14	14	16
	Cherry red	20	24	19	20
10	Bright red	18	16	17	20
	Cherry red	25	29	22	22
5	Bright red	ash fuses	26	29	ash fuses
	Cherry red	40	37	29	35

<sup>1</sup> The salts of scandium and titanium were found to affect the combustion of flour in the same way as lanthanum, yttrium, cerium, and thorium. However, the effects of these two metals were somewhat obscured because excessive amounts of nitric acid were required to hold their nitrates in solution on account of their weak basicity.



practicable to reduce the time of ashing 5 gm. of flour from about 5 hours, the time required by the A.O.A.C. method, to about 25 minutes or possibly less. Obviously a 3-gram sample can be ashed in a still shorter time by the aid of these reagents. •

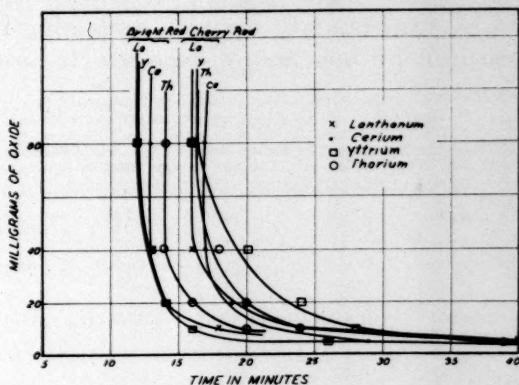


Fig. 1. Soft Wheat Flours

Under more favorable conditions for combustion, the time required for ashing flour can be reduced still further. For instance, by using a flat-bottomed silica dish 86 mm. in diameter and supplying the muffle with oxygen, we have ashed 5 gm. of flour with 20

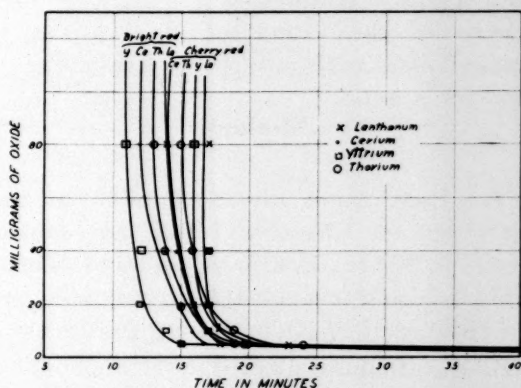


Fig. 2. Hard Wheat Flours

mg. of lanthanum oxide in  $5\frac{1}{2}$  minutes,  $4\frac{1}{2}$  of which were required for driving off the volatile matter. However, such records will probably not interest the average analyst, as they require conditions that are impractical for control work.

All the ashes were infusible at the temperatures employed except in two instances, as noted in Table II, and all were white,

rather than light gray, except those of the hard wheat flour obtained by yttrium and thorium at the lower temperature, that is, cherry red. These were light gray with a slight tinge of blue. Table III shows the relative hygroscopicity of ashes from 5 gm. of hard wheat flour containing 20 mg. of the different oxides; and of ashes obtained by the A.O.A.C. method containing none of these oxides, as measured by one hour's exposure to ordinary atmospheric conditions.

TABLE III  
INCREASE IN WEIGHT OF INCINERATED RESIDUES FOR 5 GRAMS OF HARD WHEAT FLOUR  
WITH AND WITHOUT 20 MILLIGRAMS OF THE OXIDES INDICATED

	$\text{La}_2\text{O}_3$	$\text{Y}_2\text{O}_3$	$\text{Ce}_2\text{O}_3$	$\text{ThO}_2$	A. O. A. C. Method	
					No oxide	No oxide
Weight of dish and ash immediately after removal from dessicator, gm.	20.9667	17.5418	21.1233	21.3617	21.1016	17.5227
Weight of dish and ash after one hour's exposure in open atmosphere, gm.	20.9675	17.5424	21.1241	21.3621	21.1022	17.5230
Increase in weight, gm.	0.0008	0.0006	0.0008	0.0004	0.0006	0.0003

These data show that there are no significant differences in hygroscopicity of the ashes containing the above oxides and those obtained by the A.O.A.C. method.

On the basis of the foregoing observations the following method for ashing flour with lanthanum oxide was developed.

### Method

#### Reagents

**Solution A.**—Lanthanum nitrate in 40% alcohol containing 0.75 mg.  $\text{La}_2\text{O}_3$  per cc. (dissolve 1.9925 gm. lanthanum nitrate  $[\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$  in 800 cc. of 40% alcohol and dilute to one liter.) Ten cc. of this solution evaporated to dryness and incinerated should leave a residue of  $\text{La}_2\text{O}_3$  weighing 0.0075 gm.

**Solution B.**—Lanthanum nitrate in 40% alcohol containing 1.5 mg.  $\text{La}_2\text{O}_3$  per cc. (dissolve 3.985 gm. of the nitrate in 800 cc. of 40% alcohol and dilute to one liter.) Ten cc. of this solution evaporated to dryness and incinerated should leave a residue of  $\text{La}_2\text{O}_3$ , weighing 0.015 gm.

#### Determination

Into an ignited, tarred, flat-bottomed silica dish, 65 mm. in diameter or larger, weigh 5 gm. of flour. Spread flour evenly over

the bottom of the dish. For soft wheat flour add 10 cc. of solution A; for hard wheat flour, add 10 cc. of solution B. By means of a light-weight stirring rod, bent at a right angle 1 cm. from the end, mix and work the solution into the sample until a uniform paste results, entirely free from lumps. Wipe the stirring rod with a small piece of ashless filter paper and add the paste to the sample.

TABLE IV

COMPARISON OF RESULTS OBTAINED BY ASHING 5-GRAM SAMPLES OF A SOFT WHEAT FLOUR WITH LANTHANUM OXIDE AND BY THE A. O. A. C. METHOD

Sample	Lanthanum Method		Sample	A. O. A. C. Method	
	Net weight of ash	Percentage of ash		Net weight of ash	Percentage of ash
	gm.			gm.	
1	0.0196	0.392	1	0.0195	0.39
2	.0201	.402	2	0.0208	.416
3	0.0195	.39	3	0.0207	.414
Average	.....	0.395	Average	.....	0.406

Place dish and contents directly into a muffle furnace heated to a bright cherry red. Leave in furnace until a carbon-free ash results (25 to 30 minutes). Cool in a desiccator and weigh, correcting the result by subtracting the weight of the  $\text{La}_2\text{O}_3$  added.

Tables IV and V show how duplicated results obtained by the above method check each other and how results obtained by this method compare with those obtained by the A.O.A.C. method.

TABLE V

COMPARISON OF RESULTS OBTAINED BY ASHING 5-GRAM SAMPLES OF A HARD WHEAT FLOUR WITH LANTHANUM OXIDE AND BY THE A. O. A. C. METHOD

Sample	Lanthanum Method		Sample	A. O. A. C. Method	
	Net weight of ash	Percentage of ash		Net weight of ash	Percentage of ash
	gm.			gm.	
1	0.025	0.50	1	0.0214	0.428
2	0.025	.50	2	0.0207	.414
3	0.0241	.482	3	0.0214	.428
Average	.....	0.492	Average	.....	0.423

The lower ash values obtained on the soft wheat flour by the use of lanthanum oxide are probably due to the elements of water that are eliminated by the union of the oxide with the ash. With the hard wheat flour the higher ash values obtained by the use of lanthanum oxide are in all probability due to acid radicals that are bound by the lanthanum oxide and volatilized by the A.O.A.C. method from ashes that are as strongly acid as those of hard wheat flour. With such flours the loss in water is more than compensated for by acid radicals so held.

The writer is indebted to Dr. O. S. Rask for helpful suggestions in the preparation of this paper.

## DETERMINATION OF ASH BY DIRECT WEIGHING

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Read at the meeting of the Pioneer Section of the A.A.C.C. at  
Newton, Kansas, November, 1928

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Much discussion and prejudice has existed in the past concerning the merits of the direct ash determination. As no articles or data substantiating the claims or faults of the direct ash method had been published, at the time my investigation was started, I decided to ascertain the true facts of the case.

The two methods most commonly used in the Southwest for routine ash determination of wheat flour will be discussed. These are the standard A.O.A.C. method and the direct ash method. While this paper is primarily a discussion of the direct ash determination, it will be necessary to give briefly my experience with the A.O.A.C. method in order that a standard of comparison may be had and to illustrate wherein the direct method is superior to the A.O.A.C. method.

In brief, the procedure for both methods is as follows: (1) For the A.O.A.C. method, 3 grams of flour is weighed into an accurately weighed crucible that has been previously ignited and cooled to room temperature in a desiccator. The flour is then incinerated at the proper temperature to a fluffy white or gray-white ash. The crucible and ash are then cooled to room temperature in a desiccator and accurately weighed. The difference between the final weight and the original weight is the weight of the ash from which the percentage is calculated. (2) For the direct ash method, the 3 grams of flour are weighed into a perfectly balanced aluminum scoop. The flour is then transferred carefully to a clean crucible and incinerated to a fluffy white or gray-white ash. The crucible and ash are then cooled in a desiccator to room temperature, the ash is dumped out of the crucible onto the pan of the balance, and the direct weight is obtained.

In my investigation only the silica crucibles size 0 were used.

I had observed in my experience with the A.O.A.C. method that a variation existed in ash results and checks that could not be eliminated by careful and accurate balance work. It was at first thought that this variation was due to the hygroscopic properties of the ash and that the ash absorbed moisture while cooling in the desiccator or while being weighed out. Several desiccating



agents had been tried to overcome this variation, and calcium carbide was finally selected as the most satisfactory. However, the variation persisted in spite of the care taken to obtain uniform results.

During rush seasons I had adopted the practice of taking out of the muffle, during slack periods of the day, the approximate number of crucibles that I would need for the next day and obtaining the weights on them, then replacing them in the desiccator until needed. I soon noticed, upon checking the weights of the crucibles, that they often did not agree with the original weights obtained, but had for the most part gained in weight. Table I illustrates the change in weight of the crucibles that took place in the desiccator.

TABLE I  
CHANGE IN WEIGHT OF CRUCIBLES UPON STANDING IN THE DESICCATOR

Group	Original weight of crucible	Weight of crucible after standing in desiccator	Gain in weight
	grams	grams	grams
1	10.7350	10.7353	0.0003
	10.6778	10.6782	.0004
	10.6553	10.6537	.0004
2	12.3892	10.3890	— .0002
	10.4956	10.4954	— .0002
	11.4785	11.4783	— .0002
3	13.0003	13.0003	.0000
	13.3621	13.3621	.0000
	8.1467	8.1467	.0000
4	12.7685	12.7685	.0000
	12.3892	12.3894	.0002
	10.4956	10.4959	0.0003

This change in weight was seldom the same for the various groups or for the crucibles in the groups. A noteworthy characteristic was that the change in weight was usually less in the first crucible to be weighed out of a group than in the last. This change is apparently due to a film of moisture being absorbed upon the surface of the silica crucibles, thus changing their weight. Liddel<sup>1</sup> has noted this characteristic and has observed that the variation in weight varied directly with the humidity. That is, if the humidity was low when the original weight was taken and high when the second weight was taken, the second weight would be greater than the first. Any change in weight of the crucible in the desiccator would affect the accuracy of the ash determination by the A.O.A.C. method.

<sup>1</sup> Cereal Chem. 6: 134-139 (1929).

In the direct ash method, the weight of the crucible does not enter into the calculation of the percentage of ash. Therefore if flour could be incinerated so that the ash would not fuse or stick to the crucible and could be completely removed, the direct method should give more uniform results. On first thought it might appear that an error would be introduced in weighing the flour in a scoop and transferring it to the crucible. However, an error of one milligram would affect the percentage only in the fourth decimal place. It would take an exceedingly careless analyst to make a greater error than one milligram in weighing and transferring the flour to the crucible. If he were that careless, his results would be questionable by any method.

In obtaining data that would give a close comparison between the A.O.A.C. method and the direct method, I chose a method that would eliminate any variation due to a possible non-uniformity of the sample. The procedure was as follows: The crucibles were

TABLE II  
COMPARISON BETWEEN A. O. A. C., DIRECT, AND A. O. A. C. WITH CORRECTED CRUCIBLE WEIGHT

Ash, A. O. A. C.	Ash, direct	Ash, A. O. A. C. with corrected crucible weight
%	%	%
0.450	0.450	0.450
.453	.440	.440
.503	.493	.490
.450	.450	.450
.400	.400	.400
.840	.840	.837
.407	.410	.403
.457	.447	.447
.457	.460	.457
0.397	0.380	0.383

ignited, then cooled to room temperature in a desiccator and carefully weighed soon after reaching room temperature. Three grams of flour was then weighed in the crucibles and incinerated to a fluffy ash. The ash and crucibles were then cooled to room temperature in a desiccator and weighed. As soon as the weight of the crucible and ash was obtained, the ash was dumped upon the balance pan and its weight obtained. Then the crucible was weighed without the ash. This final weight of the crucible was called the corrected weight and the ash percentage was calculated from it as well as from the original weight of the crucible. Figures in Table II are typical of the ash percentages obtained from the foregoing procedure and were taken from 42 determinations made along with the regular routine ash determinations over a period of two weeks.

The complete list compared in the following ratio: 28.6%

A.O.A.C. percentages checked exactly with the direct method; 59.5% A.O.A.C. percentages varied from 0.003 to 0.010%; and 11.9% A.O.A.C. percentages varied from 0.010 to 0.017%. This gives a total of 88.1% A.O.A.C. percentages varying from exact checks to 0.010%, which is considered by many to be a good check for ash determination.

The comparison between percentages by the direct ash method and by the A.O.A.C. method, figured from the corrected weight of the crucibles, gave 45.2% exact checks, 45.2% differed by 0.003%, and 9.6% differed by 0.007%. This gives 90.4% that varied from exact checks to a variation of 0.003%, which is excellent. Or 100% varied from exact checks to a maximum variation of 0.007%, which is very good.

TABLE III

COLLABORATING RESULTS OF ASH IN WHICH FOUR LABORATORIES USED THE DIRECT METHOD AND ONE LABORATORY USED THE A. O. A. C. METHOD

Lab. A Direct	Lab. B A. O. A. C.	Lab. C Direct	Lab. D Direct	Lab. E Direct	Av.	Max. spread
%	%	%	%	%	%	%
0.437	0.440	0.433	0.433	0.433	0.435	0.007
.417	.425	.420	.417	.417	.419	.008
.393	.405	.399	.400	.400	.400	.012
.415	.420	.417	.410	.413	.415	.010
.415	.400	.413	.418	.420	.413	.020
.403	.400	.400	.400	.400	.401	.003
.363	.373	.360	.360	.367	.365	.013
0.410	0.415	0.417	0.413	0.413	0.417	0.007

I have used the direct ash method in daily routine for more than a year on both the 1927 and the 1928 crop, and the maximum variation on duplicate was 0.003%, which is an excellent record for the method. A 0.003% variation can be considered as good as an exact check, since the balance that I use is sensitive to one-tenth of a milligram. With the A.O.A.C. method a variation of 0.010% was not uncommon on duplicate determinations.

It is the practice of the Kansas City laboratory of the Larabee Flour Mills Co. to send weekly check samples of flour to the mill laboratories for ash, moisture, and protein checks. On these check samples, four of the laboratories used the direct ash method and one laboratory used the A.O.A.C. method. I have compiled a list of 29 consecutive ash checks covering a period of eight months. Table III is taken from this list.

The completed list compares in the following ratio: 55.6% checked from 0.003 to 0.010% inclusive, 37.0% checked from 0.012 to 0.020% inclusive, and 7.4% checked from 0.030 to 0.031%. The sum total gives 92.6% checking from 0.003 to 0.020%. This is considered very good for collaborating laboratories. For purposes of

comparison the spread between the highest and the lowest results obtained by the Pioneer Section of the A.A.C.C. for the last eight months have been recorded in Table IV.

TABLE IV  
MAXIMUM SPREAD OF ASH OBTAINED BY THE PIONEER SECTION OF A. A. C. C. ON THEIR MONTHLY COLLABORATING CHECK SAMPLE

July	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.
%	%	%	%	%	%	%	%
0.058	0.045	0.049	0.036	0.046	0.033	0.053	0.042

This gives an average spread of 0.045%. However, as at least four different methods for ash determination are used by the members of the Pioneer Section, closer checks than given in Table IV could hardly be expected.

### Summary

In the direct ash method no difficulty has been experienced from the ash sticking to the crucible so badly that it could not be knocked loose by tapping the crucible lightly on the table or with the spatula. The temperature at which the ash is incinerated is important in preventing sticking. This temperature varies for flours from various sections of the country and can be best determined by trial. The muffle temperature best suited for the 1928 crop of the Southwest section is about 1000° F. A chemical balance that is accurate within one-tenth of a milligram is necessary for accurate results. The hygroscopic property has been found to be within the limit of sensitivity of the chemical balance used. Ash has been left on the balance pan for 10 minutes with no detectable change in weight. However, this characteristic may not be true for ash from flour from other than the Hard Winter wheat territory. At any rate, the increased speed in weighing out the ash in the direct method will hold any error from the hygroscopic property of the ash down to the minimum.

### Conclusions

The following conclusions have been drawn from the data and subject matter given in this paper.

1. The direct ash method is less susceptible to error due to the personal factor, because only one exact weighing, that of the ash residue, is necessary.
2. Errors due to variations of humidity are eliminated in the direct method, the hygroscopic properties having been found to be within the limit of sensitivity of the balance.



3. The direct method gives better and more uniform checks for both individual and collaborating laboratories.

4. The time factor in weighing in the flour and weighing out the ash has been reduced from one-half to two-thirds that required by the A.O.A.C. method.

### Acknowledgments

The author wishes to thank W. L. Heald, chief chemist of the Larabee Flour Mills Co., for permission to use the data from collaborative work of the laboratories; also to thank W. V. Van Scoyk, chairman of the Pioneer Section of the A.A.C.C., for permission to use data from their collaborative work.

## QUICK ASH DETERMINATION BY MAGNESIUM ACETATE-ALCOHOL METHOD

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Read at the November 1928 meeting of the Pioneer Section of A.A.C.C. at Newton, Kansas

(Read at the Convention May, 1929)

The magnesium acetate-alcohol method is an outgrowth of the author's experiences with the oxygen-acetate method as given by Brendel (1926).<sup>1</sup> There were objections to the oxygen-acetate method, such as the hygroscopic property of the calcium oxide in the ash, the high muffle temperature, and the method of applying the calcium acetate solution. This method has overcome, to a large extent, these objections.

The procedure and apparatus for the method are as follows:

**Solution.**—For each 100 cc. of solution, dissolve 1.61 grams of  $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4 \text{H}_2\text{O}$  (magnesium acetate) in 95% ethyl alcohol. Also add a few crystals of iodine, or enough to give the solution a light amber color. Filter and let stand over night before using.

**Muffle.**—Same type as used for the standard method of ash determination. Muffle temperature should be approximately  $1100^\circ$  to  $1150^\circ \text{F.}$ , or just a low red heat.

**Crucibles.**—Porcelain or silica of 10 to 15 cc. capacity, low form, and thin walls for the porcelain crucibles.

<sup>1</sup> Brendel, G. L. Oxygen-Acetate Method of Ash Determination in Flour. Cereal Chem., 3: 222-226.

**Oxygen.**—Oxygen in tank with pressure-reducing valve, pressure gauges, and applied with an oxyacetylene torch into the rear of the muffle.

### Directions

Obtain the weight of an empty crucible for a blank. Weigh 3 grams of flour to be tested into a crucible of known weight. Also weigh in 3 grams of a flour of known ash, for a control. To the flour samples and weighed crucible for blank, pipette 3 cc. of MgAc solution and see that the entire surface of flour exposed is completely wetted. Ignite after standing for about 30 seconds and burn off most of the alcohol, then place the samples, while still burning, in the middle part of the muffle. Place the blank in the cooler part of the muffle, in the front, after the flame has ceased and the blank has been carefully dried on the door, or in the front part of the muffle with the door open. The oxygen may be turned on as soon as the samples are placed in the muffle, and the muffle door closed as soon as the flame dies down enough to burn without excessive smoking. The oxygen is applied at a pressure of one pound, or the first unit mark of the scale of the low-pressure gauge. The flow, or volume, of the oxygen is controlled by either the needle valve in the torch or the needle valve at the outlet of the pressure-reducing valve. After the needle valve has been satisfactorily adjusted, it should not be changed from one burning to another. The only adjustment that needs to be made is the one that maintains the pressure. The way to tell when the needle valve is right and a large enough volume of oxygen is flowing through the muffle is to try a 3-gram sample (that has had the MgAc solution added to it and the alcohol burned off), place the sample in the muffle, and burn it in the presence of the oxygen. The time required for the burning should be about 15 minutes. If less time is taken, too much oxygen is being used. If more than 20 minutes is required, not enough oxygen is being applied. If the ash has a fused appearance at the end of a 15-minute burning, the muffle is too hot. In burning the samples, the oxygen is continued until the glow at the bottom of the crucibles has disappeared, or until the bottom of the crucibles is the same color as the floor of the muffle and not readily discernible from it. These observations are made through the peep hole in the door of the muffle without disturbing the ash or the flow of oxygen. When the ash is burned, turn off the oxygen before removing the ash, otherwise it will be blown away. Place the ash and the blank in a desiccator of vacuum

type to cool. Calcium carbide is the most satisfactory desiccant to use in the desiccator. When the ash is cool, weigh and subtract the blank and calculate as usual. The control is used as a check against the blank and also as a comparison between this method and the standard method of burning.

### Discussion and Technic

The best and most uniform results have been obtained with a MgAc solution that gives 0.0034 gram of MgO per cc. of solution burned, or 0.0034 gram of MgO for each gram of flour in the sample. The blank from this solution for a 3-gram sample should weigh close to 0.0100 gram. A solution much stronger than the one recommended will form a crust on the sample when the alcohol is burned off and will burn in a crackling manner with some loss of MgAc. A much weaker solution will not prevent the fusing of the ash. The flour will absorb the alcohol solution very rapidly, much the same as blotting paper does water, hence mixing of the solution and flour is not necessary. Also cindering the flour before adding the solution is not necessary.

The iodine is to stabilize the solution and keep it clear. Without it, the solution would become cloudy and a fungous growth would appear at the bottom of the solution, necessitating filtering every few days. The amber color due to the iodine will disappear in 48 hours, leaving a bright clear colorless solution. While the iodine is thus combined, it is still effective, as the solutions have remained proof against the growth of bacteria and clear for over a month, although used daily and exposed to wild bacteria of the air.

The ash and the blank will maintain a constant weight and not absorb enough water or carbon dioxide of the air to affect the weighing out of the samples. The MgAc ash has maintained a constant weight for 10 minutes on days when the ash obtained by the standard method would gain weight in just a few swings of the balance pointer. This characteristic eliminates guess work in the weighing out of the ash and makes the method adaptable to quantity production, being limited only to the number of crucibles that the muffle will hold at a time. After the operator has become accustomed to the method, he should, with proper care, be able to check the standard ash within 0.010 per cent. A wider variation than 0.010 per cent indicates that something is wrong and an investigation should be started to locate the trouble. If the oxygen is applied through too fine a hole in the torch, it will have too high

a velocity in passing through the muffle and blow some of the ash out of the crucibles. If care is not taken in drying and placing the blank, it will spatter when the MgAc melts before decomposing to the oxide, thus making the blank run low and the ash that is figured from the blank to run high. If care is not taken in removing the ash from the muffle, the movement through the air may be fast enough to create a current of air that will blow some of the ash out of the crucible. Care should be taken in opening and removing the lid of the desiccator for the same reason. In other words, the magnesium acetate ash is very fluffy and cannot be handled roughly. The overburning of the ash, that is, leaving the ash in the muffle for a long time after the glow has ceased, may cause the ash to run low, as it tends to disintegrate and be more susceptible to blowing.

TABLE I

COMPARISON OF ASH BY A. O. A. C. METHOD AND MAGNESIUM ACETATE-ALCOHOL METHOD

Blank	Ash, per cent	
	A.O.A.C. method	MgAc-Alcohol method
0.0099	0.453	0.453
.0100	.407	.410
.0098	.430	.440
.0099	.370	.373
.0101	.410	.410
0.0096	0.453	0.453

The concentration of solution given works as well on low grade flour as on patent, the resulting ashes differing only in color. In physical appearance the ashes are very fluffy, white to blue-gray depending upon the grade of flour. The patent flour takes longer in burning than the clear or low grade.

The flour used for the control should be one on which one or more determinations of ash by the standard method have been obtained. The control should be kept in an air-tight container in order to maintain a uniform ash content. It is advisable to check the ash of the control once a week, by the standard method, if it is used daily.

A blank must be determined for each determination, as an alcoholic solution will not maintain a constant density because of variations in temperature. If platinum crucibles are used, the blank must be calculated from the control, as MgAc will melt too fast and spatter, owing to the more rapid transfer of heat of the crucible. If desired, the blank can be calculated from the control, when porcelain or silica crucibles are used.



Table I illustrates the variation in blanks that may be expected and the degree of checking with the standard A.O.A.C. method of ash determination. The data in Table I were taken from regular routine determinations run on different days.

### ERRATUM

#### A STATISTICAL STUDY OF COLLABORATIVE PROTEIN DETERMINATIONS

ALAN E. TRELOAR

Equation (ii) on page 436 of Vol. VI, No. 5, of this Journal (September, 1929) should be corrected to read as follows:

$$\sigma_x = \sqrt{\frac{\sum (x)^2}{N} - (\bar{x})^2}$$